

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) Publication number:

0 563 414 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92105469.8**(51) Int. Cl.⁵: **B01J 23/52, B01J 31/04,
B01J 37/02, B01J 37/06,
B01J 67/055**(22) Date of filing: **30.03.92**(43) Date of publication of application:
06.10.93 Bulletin 93/40(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE(71) Applicant: **UNION CARBIDE CHEMICALS &
PLASTICS TECHNOLOGY CORPORATION
39 Old Ridgebury Road
Danbury, Connecticut 06817-0001(US)**(72) Inventor: **Bartley, William J.
500 Sheridan Circle
Charleston, West Virginia 25314(US)**(74) Representative: **Weinhold, Peter, Dr. et al
Patentanwälte Dr. V. Schmied-Kowarzik
Dipl.-Ing. G. Dannenberg
Dr. P. Weinhold
Dr. D. Gudel
Dipl.-Ing. S. Schubert
Dr. P.
Barz
Siegfriedstrasse 8
D-80803 München (DE)**(54) **Alkenyl alkanoate catalyst process.**

(57) This invention provides a process for producing improved catalysts for the production of alkenyl alkanoates by the reaction of an alkene, an alkanoic acid and an oxygen-containing gas. The catalysts contain palladium, gold and a potassium promoter and are characterized by a reduced sodium content which results in increased catalyst activity. The general invention consists of three Embodiments (i.e., Embodiment A, Embodiment B and Embodiment C). In Embodiment A, the reduced sodium content is obtained by using essentially sodium-free starting materials in the process for producing the catalysts. In Embodiment B, the reduced sodium content is obtained by washing the catalyst with water or with an aqueous solution of a potassium promoter after it has been impregnated with a potassium promoter. In Embodiment C, the reduced sodium content is obtained by washing the catalyst, at a particular intermediate point in its production, with a cation exchange solution.

EP 0 563 414 A1

BEST AVAILABLE COPY

This invention relates to a process for producing catalysts (hereinafter referred to as "alkenyl alkanoate catalysts") for the production of alkenyl alkanoates from alkenes, alkanoic acids and an oxygen-containing gas.

Processes for producing alkenyl alkanoate catalysts are known.

5 By way of illustration, U. S. Patent 4,048,096 (Bissot) discloses a catalyst having a specific activity of at least about 83 grams of vinyl acetate per gram of precious metal per hour measured at 150 °C. The Bissot vinyl acetate catalyst consists essentially of: (1) a catalyst support having a particle diameter of from about 3 to about 7 mm and a pore volume of from about 0.2 to about 1.5 ml./g., a 10% by weight water suspension of the catalyst support having a pH of from about 3.0 to about 9.0; (2) a palladium-gold alloy distributed in a surface layer of the catalyst support, the surface layer extending less than about 0.5 mm from the surface of the support, the palladium in the alloy being present in an amount of from about 1.5 to about 5.0 grams per liter of catalyst, and the gold being present in an amount of from about 0.5 to about 2.25 grams per liter of catalyst, and (3) from about 5 to about 60 grams per liter of catalyst of alkali metal acetate. Bissot discloses that the palladium is the active catalyst metal and the gold is a catalyst promoter.

15 Bissot also discloses a process for preparing the Bissot catalyst. Like Kronig et al., the Bissot process involves precipitation of the metal salts on the catalyst support. The Bissot process comprises: (1) impregnating the catalyst support with aqueous solution of water-soluble palladium and gold compounds, (2) precipitating water-insoluble palladium and gold compounds on the catalyst support by contacting the impregnated catalyst support with a solution of compounds (preferably sodium metasilicate) capable of reacting with the water-soluble palladium and gold compounds to form water-insoluble palladium and gold compounds, (3) converting the water-insoluble palladium and gold compounds into palladium and gold metal on the support by treatment with a reducing agent, (4) washing the catalyst with water, (5) drying the catalyst (see Example 1 of Bissot), (6) impregnating the catalyst with alkali metal acetate promoter (e.g., a potassium promoter), and (7) drying the catalyst.

25 The improvement disclosed in Bissot involves distributing the palladium and gold as an alloy in a surface layer of the catalyst support, the surface layer extending less than about 0.5 millimeter from the surface of the support. The impregnating step is carried out with an aqueous solution of palladium and gold compounds and the total volume of the solution is from about 95 to about 100% of the absorptive capacity of the catalyst support. The precipitating step in Bissot is carried out by soaking the wet catalyst support with a solution of an alkali metal silicate, the amount of alkali silicate being such that, after the alkali metal silicate solution has been in contact with the catalyst support for about 12 to 24 hours, the pH of said solution is from about 6.5 to about 9.5.

Bissot does not report the sodium content of the catalysts of the Bissot Examples. Bissot Example 1 reports that the catalyst of that Example had an activity of 560 grams of vinyl acetate per liter of catalyst per hour. In Example III below, two catalysts produced following the disclosure of Example 1 of Bissot were found to have sodium contents of 0.32 and 0.38 weight percent and activities of 551 and 535 grams of vinyl acetate per liter of catalyst per hour.

Despite the prior art processes, it is desirable to further improve the activity of alkenyl alkanoate catalysts.

40 In general, this invention provides a process for producing improved catalysts for the production of alkenyl alkanoates by the reaction of an alkene, an alkanoic acid and an oxygen-containing gas. The catalysts contain palladium, gold and a potassium promoter and are characterized by a reduced sodium content which results in increased catalyst activity. The general invention consists of three Embodiments (i.e., Embodiment A, Embodiment B and Embodiment C) which are described in detail below.

45 In Embodiment A of this invention, the reduced sodium content is obtained by using essentially sodium-free starting materials in the process for producing the catalysts.

In Embodiment B of this invention, the reduced sodium content is obtained by washing the catalyst with water or with an aqueous solution of a potassium promoter after it has been impregnated with a potassium promoter.

50 In Embodiment C of this invention, the reduced sodium content is obtained by washing the catalyst, at a particular intermediate point in its production, with a cation exchange solution.

SUMMARY OF EMBODIMENT A OF THE INVENTION

55 Embodiment A of this invention is based, in part, on the discovery that the activity of alkenyl alkanoate catalysts is increased if their sodium content is decreased by employing essentially sodium free starting materials in producing the catalyst.

More specifically, Embodiment A of this invention provides a process for producing a catalyst that is useful in catalysing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanolate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate:

5 said process comprising the steps of:

- (a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;
 - (b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;
 - 10 (c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent;
 - (d) washing the support particles with water;
 - (e) drying the support particles;
 - (f) further impregnating the support particles with a potassium promoter; and
 - 15 (g) drying the impregnated particles to produce the catalyst;
- and said process being conducted by employing essentially sodium-free starting materials in steps (b) and (c) so as to reduce the amount of sodium in the catalyst and thereby to increase the activity of the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS ILLUSTRATING EMBODIMENT A

20

Figure 1 shows the predicted effect of sodium on the performance of vinyl acetate catalysts produced in accordance with Embodiment A of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF EMBODIMENT A

25

In the practice of Embodiment A of the process of the present invention, sodium-containing, water-soluble palladium and/or gold compounds can usually be employed since they are usually not used in amounts that result in catalysts having substantial amounts of sodium. The principal sources of sodium in alkenyl alkanolate catalysts are sodium-containing precipitating agents (e.g., sodium metasilicate) and/or sodium-containing promoters or activators (e.g., sodium acetate). To a lesser extent, some supports and some reducing agents (e.g., sodium borohydride) can introduce substantial amounts of sodium into the catalyst. Accordingly, in the practice of this invention, essentially sodium-free precipitating agents (e.g., potassium hydroxide), promoters (e.g., potassium acetate), reducing agents (e.g., hydrazine) and carriers are employed. When using potassium hydroxide as the precipitating agent, a suitable potassium salt (e.g., potassium acetate) can also be used in the precipitating step to aid in displacement by potassium of any sodium bound on the carrier. Preferably the potassium hydroxide and the potassium salt are employed in an aqueous solution. The salt is used in an amount that provides from 1 to 10 weight percent potassium based on the total weight of the solution. Care should be exercised to ensure that the resulting catalyst does not contain so much potassium that catalyst activity is less than desired.

40 The support particles used in Embodiment A of the process of this invention are solid particulate materials that are capable of exchanging cations (e.g., due to the presence of SiOH or AlOH groups), that are capable of being impregnated with palladium, gold and a potassium promoter and that are inert under the conditions used to produce alkenyl alkanolates. Illustrative of such support particles are particulate silica, alumina, and silica-aluminas. Silica is the preferred support. The support preferably has a surface area from 100 to 800 square meters per gram.

45 The aqueous solutions of water-soluble palladium and gold compounds used in Embodiment A of the process of this invention include aqueous solutions of any suitable palladium or gold compound such as palladium (II) chloride, sodium tetrachloropalladium (II) (Na_2PdCl_4), palladium (II) nitrate, palladium (II) sulfate, gold (III) chloride or auric (III) acid (HAuCl_4). The volume of the solution preferably corresponds to from 95 to 100% (more preferably from 98 to 99%) of the pore volume of the support.

50 The precipitating agents used in Embodiment A of the process of the present invention include lithium and potassium silicates and hydroxides. The precipitating agents are preferably employed in the form of aqueous solutions containing a 1.6 to 1.8 molar excess of the precipitating agents. The volume of such solution used is preferably just sufficient to cover the support particles. To avoid possible degradation of the support, the weight ratio of the precipitating agent to the support should not be too high. By way of illustration, a weight ratio of potassium hydroxide to support of about 0.08:1 resulted in no noticeable degradation of the support.

The reducing agents used in Embodiment A of the process of this invention include ethylene, hydrazine, formaldehyde and hydrogen. The reducing agents are preferably employed in the form of aqueous solutions containing a 50:1 (or more preferably a 10:1) molar excess of the reducing agents. If hydrogen is used, it is usually necessary to heat the catalyst to 100 to 300 °C to complete the reduction.

5 The potassium promoters used in Embodiment A of the process of this invention include potassium alkanoates and any potassium compound that is converted to a potassium alkanoate during the alkenyl alkanoate-forming reaction (i.e., the reaction of ethylene, an alkanolic acid and an oxygen-containing gas in the presence of the catalyst to produce an alkenyl alkanoate). Suitable potassium compounds include potassium acetate, bicarbonate, nitrate and (when a stable support is used) hydroxide. The promoters are
10 preferably applied in the form of aqueous solutions.

The washing step in Embodiment A of the process of this invention can be conducted batchwise or continuously. Continuous washing is more efficient but may not be most suitable for large scale (e.g., plant scale) catalyst production. In continuous washing, the wash water is slowly and continuously passed through the catalyst over a period of time (e.g., from 8 to 24 hours). In batch washing, the catalyst is contacted with
15 the wash water, the mixture is allowed to stand (e.g., for from 0.5 to 2.0 hours) and the water and catalyst are separated. In batch washing, several such washes (e.g., from 2 to 10, or preferably from 4 to 6 washes) are often required to reduce the impurity (e.g., halide) content of the catalyst to the desired level. Temperatures from 20 °C to 80 ° and volume ratios of wash water to catalyst of from 2:1 to 100:1 can be used in either batch or continuous washing. The washing step removes certain impurities, particularly
20 chlorides, from the catalyst.

The drying of the catalyst in accordance with step (e) and step (g) of Embodiment A of the process of this invention for producing alkenyl alkanoate catalysts can be conducted in any convenient manner. By way of illustration, drying can be conducted at 40 °C to 120 °C in a forced air oven for 15 to 30 hours.

25 EXAMPLES OF EMBODIMENT A

In the following Examples, the following abbreviations are used:

30

35

40

45

50

55

<u>Abbreviation</u>	<u>Meaning</u>
Support I	Silica beads having an average diameter of 5 to 6 millimeters and containing about 0.1 weight percent sodium. The beads have a surface area from 150 to 200 square meters per gram and a pore volume from 0.6 to 0.7 milliliters per gram. Support I contains SiOH groups that are capable of exchanging cations. Support I is sold by Sud Chemie AG as "KA-160"
STY*	Space Time Yield (a measure of catalyst activity) expressed as grams of vinyl acetate per liter of catalyst per hour.
% Selectivity*	Selectivity was calculated as follows: $\text{Selectivity} = 100 \times (\text{moles vinyl acetate}) / (\text{moles vinyl acetate} + 1/2 \times \text{moles CO}_2)$
AA Analysis	Atomic Adsorption Spectroscopy
ICP	Inductively Coupled Plasma Optical Emission Spectrometry
g VA/l cat/hr	Grams of vinyl acetate produced per liter of catalyst per hour

*All the values for activities and selectivities reported in the Examples appearing below are based on the activities and selectivities measured twenty-six hours after full oxygen feed was reached in the Catalyst Test Method described below.

	VA	vinyl acetate
	KOAc	potassium acetate
5	EtOAc	ethyl acetate
	NaOAc	sodium acetate
10	%	percent by weight
	g	grams
	ml	milliliter
15	mm	millimeter
	hrs	hours
20	min	minute

In the following Examples, the following procedures were used:

Catalyst Preparation Procedure

Support I (15 g) was added to a solution of Na_2PdCl_4 (35.86% Pd, 0.258 g) and HAuCl_4 (48.95% Au, 0.094 g) dissolved in 9.0 ml of deionized water. The mixture so formed was gently agitated until all of the moisture was absorbed into the support and then was allowed to stand in a sealed flask for about one hour at room temperature so as to impregnate the support with the palladium and gold salts. The damp catalyst was covered with a solution of potassium hydroxide (0.371 g in 28 ml water) as a precipitating agent. Potassium acetate is used in conjunction with potassium hydroxide in the precipitation step in a preferred embodiment of this invention. After mixing for a few seconds, the mixture was allowed to stand covered and undisturbed for 23 hours at room temperature to deposit water-insoluble palladium and gold compounds on the support. The palladium and gold were then reduced by the addition of 1.0 g of 85% hydrazine hydrate to the above mixture. The mixture was agitated for a few seconds and allowed to stand covered and undisturbed at room temperature for another 23 hours. The supernatant liquid was decanted from the catalyst and the catalyst was rinsed four times with water to remove the small amount of metal sludge present. The catalyst was washed thoroughly by the Column Washing Procedure described below to remove chlorides and residual reagents. The catalyst was dried on a stainless steel screen at 60°C in a forced air oven for 20 to 24 hours. The catalyst was analyzed for potassium using AA Analysis. Then the catalyst was impregnated with the desired amount of potassium acetate in water using the impregnation technique described above for the palladium and gold salts. Then the impregnated catalyst was dried at 60°C for 20 to 24 hours. The palladium, gold, sodium, and potassium contents in the finished catalysts were determined by ICP analyses and the sodium and potassium contents were also determined by AA Analyses for greater accuracy. The catalysts so produced were shell-impregnated (i.e., substantially all of the palladium and gold was present in a shell within 0.5 mm of the surface of the beads of Support I).

Column Washing Procedure

Catalysts were washed or rewashed in a 1.24 inch o.d. x 24 inches glass chromatography column fitted with a Teflon™ stopcock. Typically 15 g of catalyst was added to the column which was then filled with water. The stopcock was adjusted to allow the liquid to flow from the column such that about one liter passed through the catalyst at room temperature over a period of about 24 hours. After this period, the excess liquid was drained from the column and the catalyst removed and dried as described above in the Catalyst Preparation Procedure.

Catalyst Test Method

The catalyst (2.5 g samples of 5 to 6 mm catalyst spheres) was diluted with 10.5 ml of 0.5 mm glass beads and the mixture was uniformly distributed in both legs of a 316-stainless steel U-tube reactor. The reactor had an outside diameter of 3/8 inch and an overall height of about 6 inches. An ethylene flow of 151 ml/min. was started through the reactor after which the catalyst was heated in an oven maintained at 150 °C while allowing the system to pressurize to 115 psig. After maintaining at these conditions for 1.5 hours, acetic acid vapor was added to the ethylene and the mixture was passed over the catalyst for 45 minutes. Air was added to the feed gas at a slowly increasing rate over a 45-minute period until a total flow of 105 ml/min. was reached. The catalyst was allowed to stabilize for two hours before beginning data collection. The final gas composition was ethylene:acetic acid:oxygen:nitrogen = 52.9:10.7:7.7:28.7, the total gas hourly space velocity was about 3800 hr⁻¹, and the acetic acid liquid hourly space velocity was about 1 hr⁻¹. The product was analyzed by gas chromatography. The run-to-run reproducibility of the microreactors used in these experiments is about ±10 STY units.

EXAMPLE I

Support I contains about 0.1 weight percent sodium as received from the manufacturer. An additional 0.4 to 0.8 weight percent of sodium is introduced during the precipitation step when sodium hydroxide or sodium metasilicate is used as the precipitating agent. Three catalysts were prepared using potassium hydroxide as the precipitating agent to reduce the sodium level in the final catalyst. Varying concentrations of potassium acetate were added to the precipitating solution to further shift the ion-exchange equilibrium toward potassium. The catalysts were prepared from the same master batch having a nominal palladium loading of 0.58 weight percent and an Au/Pd ratio of 0.46. After reduction with hydrazine and washing using the Column Washing Procedure, the catalysts were analyzed for sodium and potassium. Then additional potassium acetate was added as required to give a final potassium acetate content of about 5.3 weight percent. The results given in Table A show that the sodium content of the catalysts was reduced. The sodium content in the catalysts dropped uniformly and catalytic activity improved as the potassium concentration of the precipitating solution was increased.

Table A

Low-Sodium Catalyst Preparations			
% KOAc (a)	% Na (b)	STY	% Selectivity
0	0.186	576	93.4
2.5	0.121	603	93.2
5.0	0.091	597	93.4

(a) Wt % potassium acetate added to the precipitating solution.

(b) Wt % sodium calculated to be in the finished catalyst. Based on AA Analyses prior to KOAc impregnation and the quantity of KOAc added.

A similar catalyst, prepared using sodium metasilicate as the precipitating agent (in lieu of potassium hydroxide) had an STY of 544, a selectivity of 93.6 and a sodium content of 0.44 weight percent. No potassium acetate was added in the precipitation step.

Example II

The effect of sodium on the performance of vinyl acetate catalysts was studied using statistically designed experiments and models were obtained which are useful in predicting the performance of the vinyl acetate catalysts produced by any of the embodiments of the process of this invention (i.e., Embodiments A, B and C) as well as vinyl acetate catalysts produced by the processes of the two above-mentioned U.S. patent applications filed concurrently herewith. The models predict catalyst activity and selectivity as a function of sodium content, palladium loading, gold to palladium weight ratio, potassium content and catalyst weight. These models and the data from which they were generated are shown in Tables B and C respectively.

EP 0 563 414 A1

Because the degree of conversion has a major effect on both catalyst productivity and selectivity, meaningful comparisons of catalyst variables can only be done at constant conversion. In order to predict the effects of catalyst composition at constant conversion, the Oxygen Conversion Model in Table B was rearranged to express catalyst weight as a function of the palladium content, gold/palladium ratio, potassium content, sodium content and conversion. This catalyst weight term was then used to replace the catalyst weight terms in the STY and Selectivity models. The predicted effects of increasing sodium content on vinyl acetate catalyst activity and selectivity are plotted in Figure 1. The abbreviations used in Tables B and C have the following meanings:

Pd	Weight percent palladium in the catalyst
Au/Pd	Weight ratio of gold to palladium in the catalyst
Cat.Wt	Catalyst weight in grams
K	Weight percent potassium in the catalyst
Na	Weight percent sodium in the catalyst
STY	Space time yield in grams of vinyl acetate per liter of catalyst per hour
R ²	Correlation coefficients which are indicative of the quality of fit of the data to the models
RSD	Relative standard derivation
EtOAc By-Product Rate	Production of ethyl acetate in moles/kilogram of catalyst/hour
% Heavies By-Products in VA	Heavy by-products expressed as a weight percent of the vinyl acetate produced. Heavies by-products are defined as all products which elute after acetic acid in the gas chromatographic analytical procedure.

Table D shows the effect of varying sodium on catalyst activity as predicted by the models in Table B.

TABLE B

MODELS RELATING
PERFORMANCE TO CATALYST COMPOSITION (a)

Part A

 O_2 Conversion to Vinyl Acetate = $100/(1 + e^{Z1})$

$$\text{Where } Z1 = 0.507 - 1.907(XPd-0.743) - 0.863(Au/Pd-0.584) + 0.109(ZK-2.43) + 0.459(ZNa-0.502) \\ (19.6) \quad (8.1) \quad (4.5) \quad (7.0)$$

$$- .913(Cat.Wt.-1.91) + 1.438(XPd-0.743)(Au/Pd-0.584) + 0.551(Au/Pd-0.584)(Cat.Wt.-1.91) \\ (29.8) \quad (3.9) \quad (5.1)$$

$$+ 1.438(XPd-0.743)^2 + 2.779(Au/Pd-0.584)^2 + 1.384(ZK-2.43)^2 + 0.284(Cat.Wt.-1.91)^2 \\ (3.1) \quad (4.2) \quad (4.4) \quad (6.5)$$

$$R^2 = 0.988 \\ RSD = 0.103$$

Part B

Activity (STY) = e^{Z2}

$$\text{Where } Z2 = 6.707 + 0.942(XPd-0.743) + 0.334(Au/Pd-0.584) - 0.194(ZNa-0.502) - 0.123(Cat.Wt.-1.91) \\ (13.6) \quad (5.6) \quad (4.0) \quad (8.1)$$

$$- 1.438(XPd-0.743)^2 - 0.128(ZK-2.43)^2 \\ (4.3) \quad (5.6)$$

$$R^2 = 0.972 \\ RSD = 0.079$$

Part C

Selectivity to Vinyl Acetate = $100 - e^{Z3}$

$$\text{Where } Z3 = 1.9 + 0.457(XPd-0.743) - 0.118(ZK-2.43) - 0.095(ZNa-0.502) + 0.121(Cat.Wt.-1.91) \\ (17.4) \quad (12.7) \quad (3.5) \quad (14.8)$$

$$+ 0.186(XPd-0.743)(Cat.Wt.-1.91) - 0.254(Au/Pd-0.584)(ZK-2.43) - 0.0525(ZK-2.43)(Cat.Wt.-1.91) \\ (5.9) \quad (6.3) \quad (4.6)$$

$$- 0.164(ZNa-0.502)(Cat.Wt.-1.91) + 0.038(ZK-2.43)^2 \\ (4.1) \quad (3.2)$$

$$R^2 = 0.956 \\ RSD = 0.034$$

TABLE 8 (Cont'd)

Part D
EtOAc By-Product Rate = e^{Z4}

$$\text{Where } Z4 = -3.640 + 0.9175(\text{X-Pd}-0.743) - 1.135(\text{Au/Pd}-0.584) - 0.2189(\text{Cat. Wt.}-1.91) - 0.3743(\text{ZNa}-0.502) \\ (7.5) \quad (10.7) \quad (8.1) \quad (6.4)$$

$$- 0.267(\text{X}-2.43)^2 - 2.428(\text{X-Pd}-0.743)^2 \\ (7.2) \quad (4.1)$$

$$R^2 = 0.872 \\ RSD = 0.142$$

Part E
Z Heavies By-Product in VA = e^{Z5} (b)

$$\text{Where } Z5 = 0.280 + 0.441(\text{Au/Pd}-0.584) - 0.254(\text{X}-2.43) - 0.0694(\text{Cat. Wt.}-1.91) \\ (5.2) \quad (10.5) \quad (3.1)$$

$$R^2 = 0.797 \\ RSD = 0.119$$

(a) Values in parentheses beneath the regression equations are the observed T-ratios.

(b) Based on the amount of vinyl acetate produced.

TABLE C

DESIGN DATA(a)

No.	%Pd	Au/Pd	%K	%Na	Cat. Wt.	% O ₂ Conv	STY	% Selectivity
1	0.80	0.70	2.23	0.51	1.64	34.4	897.6	93.2
2	0.80	0.70	2.23	0.51	1.65	37.1	941.5	92.9
3	0.80	0.70	2.23	0.51	1.65	34.8	923.3	93.2
4	1.05	0.91	3.67	0.26	0.73	16.1	1181.7	94.4
5	0.57	0.46	2.33	0.14	0.73	7.1	759.2	94.6
6	0.54	0.89	2.27	0.16	2.50	44.9	727.4	92.5
7	1.13	0.96	2.35	0.18	0.75	21.0	1262.4	94.1
8	0.52	0.44	3.51	0.17	0.76	5.8	553.2	94.5
9	1.14	0.46	2.35	0.19	2.50	66.1	912.3	89.7
10	0.53	0.91	3.64	0.14	2.51	32.7	595.0	94.4
11	1.05	0.47	3.68	0.18	2.50	55.7	847.4	92.1
12	1.08	0.87	2.80	0.73	0.76	17.5	1158.0	93.8
13	0.52	0.46	1.50	0.37	0.72	6.6	569.0	94.0
14	0.52	0.85	1.40	0.50	2.50	38.4	587.4	91.5
15	1.08	0.94	1.40	0.54	0.74	19.3	1111.7	92.1
16	0.55	0.42	2.70	0.44	0.76	5.9	617.2	94.3
17	1.10	0.45	1.40	0.59	2.54	57.7	769.9	89.7
18	0.55	0.91	2.90	0.40	2.54	34.7	629.5	94.1
19	1.09	0.47	2.80	0.50	2.52	56.6	865.0	91.5
20	0.82	0.70	2.12	0.49	1.63	35.2	901.9	93.0
21	0.82	0.70	2.12	0.49	1.62	35.7	925.7	92.9
22	0.78	0.65	2.12	0.53	2.52	50.6	793.2	92.2
23	0.78	0.65	2.12	0.53	1.63	33.3	884.2	93.4
24	1.07	0.83	2.93	0.69	2.53	51.8	822.1	92.5
25	0.53	0.36	2.96	0.44	2.52	28.5	506.7	93.4
26	1.07	0.82	1.47	0.56	2.50	54.3	709.7	88.7
27	1.07	0.82	1.47	0.56	2.51	52.4	701.7	89.3
28	0.56	0.82	3.02	0.42	0.75	7.7	733.8	95.0
29	1.02	0.46	2.88	0.48	0.75	14.1	966.6	93.8
30	0.54	0.44	1.51	0.36	2.50	29.6	483.5	92.7

TABLE C (Cont'd)

No.	%Pd	Au/Pd	%K	%Na	Cat. Wt.	% O ₂ Conv	STY	% Selectivity
31	0.54	0.80	1.48	0.50	0.75	10.8	763.7	94.0
32	1.08	0.43	1.47	0.63	0.75	13.1	889.6	93.2
33	0.80	0.66	2.12	0.92	1.64	33.0	871.5	93.2
34	0.80	0.66	2.12	0.92	1.62	32.3	866.6	93.5
35	1.13	0.62	2.10	0.59	1.62	43.1	1066.2	92.4
36	0.41	0.61	2.20	0.37	1.64	21.3	621.8	94.2
37	0.76	0.87	2.10	0.55	1.62	33.3	881.8	93.7
38	0.76	0.34	2.10	0.45	1.65	27.5	734.0	93.4
39	0.77	0.61	2.10	0.52	0.43	9.9	1246.7	93.7
40	0.77	0.61	2.10	0.52	2.86	56.9	745.8	91.7
Supplemental Data (b)								
41	0.56	0.39	2.19	0.44	2.54	36.0	607.8	93.5
42	0.57	0.39	2.19	0.15	2.54	38.4	612.0	92.7
43	0.54	0.39	3.38	0.68	2.54	25.8	482.8	94.1
44	0.55	0.39	3.38	0.28	2.54	30.9	545.9	93.5
45	0.56	0.39	2.79	0.28	2.54	36.4	605.5	93.4
46	0.56	0.39	2.79	0.16	2.54	37.2	610.9	92.9
47	0.54	0.39	2.79	0.96	2.54	27.4	493.2	93.8
48	0.54	0.39	3.62	0.36	2.54	27.2	492.4	93.7
49	0.57	0.39	1.95	0.20	2.54	35.3	571.0	92.9
50	0.54	0.39	3.70	0.39	2.54	27.1	483.8	93.9
51	0.55	0.39	2.12	1.25	2.54	27.4	494.1	94.1
52	0.50	0.39	3.95	2.39	2.54	13.4	283.9	94.3
53	0.56	0.39	2.25	0.50	2.54	33.6	609.3	93.5
54	0.57	0.39	2.25	0.12	2.54	34.9	641.5	93.1
55	0.55	0.39	2.25	1.01	2.54	28.7	540.0	94.1

(a) Unless otherwise indicated, the palladium and gold values were determined by ICP and the sodium and potassium values were determined by Atomic Absorption Analysis.

(b) The catalysts were prepared by addition of sodium and potassium acetates to Catalyst II that had been rewashed as described in Embodiment A of this invention. Reported compositions are calculated from the analysis of this catalyst and the quantities of sodium and potassium acetate added.

TABLE D

Predicted Effect of Sodium on Catalyst* Activity		
% Na	STY	% Improvement**
0.1	665	0.0
0.2	649	2.5
0.3	633	5.1
0.4	618	7.6
0.5	603	10.3
0.6	581	14.5
0.7	574	15.9
0.8	560	18.8
0.9	546	21.8

* For a catalyst composition set at: 0.58% Pd, Au/Pd = 0.45 and 2.2% K and an oxygen conversion set at 35%.

** Predicted percent change in STY resulting from decrease in sodium content from amount shown in first column to 0.1%.

EXAMPLE III

The procedure of Example 1 of U.S. Patent 4,048,096 (Bissot) was repeated as follows: Two preparations (Runs 1 and 2) were made, each employing 15g of Support I, 0.315 g of Na_2PdCl_4 , 0.085 g of HAuCl_4 , 0.585 g of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, 0.59 g of 85% hydrazine hydrate, and 0.823 g of potassium acetate. Since the exact washing procedure is not disclosed in Example 1 of Bissot the catalyst of Run 1 was washed using the Column Washing Procedure for 16 hours using 23 ml of H_2O per gram of catalyst whereas the catalyst of Run 2 was similarly washed but with 31 ml of H_2O per gram of catalyst. The catalysts of Runs 1 and 2 were analyzed by ICP for palladium and gold and by AA Analysis for potassium and sodium. The experimental error of the sodium determination is estimated to be about ± 0.01 relative percent. The catalyst of Run 1 was analyzed in duplicate. The results are shown in Table E.

TABLE E

	%Pd	%Au	%K	%Na	STY	Selectivity
Run 1	0.544	0.201	2.34	0.32	550	93.9
Run 1	0.556	0.204	2.35	0.32		
Run 2	0.552	0.195	2.34	0.38	535	93.7
Bissot	0.578*	0.242*	2.08*	----	560**	93**

* Calculated based on the data in Example 1 of Bissot

** Disclosed in Example 1 of Bissot

EXAMPLE IV

The measured activities of three commercial catalysts (Catalysts X, Y and Z) are shown in Table F. In Table F, the activities of Catalysts X and Y are compared to the predicted activities of catalysts of any embodiment of this invention having the same composition ("Model Catalysts"). The predicted activities were determined from the models of Table B and assuming a 0.15% level of sodium. The Model Catalysts had markedly higher predicted activities. A similar comparison could not be made for Catalyst Z because its composition is outside the range of the models of Table B.

Catalyst X was prepared using the Catalyst Preparation Procedure. The preparation of Catalyst X differed from the preparation of Catalyst Y in that, in the preparation of Catalyst Y: (1) the catalyst was dried before precipitation and (2) the precipitating agent used was sodium hydroxide rather than sodium metasilicate. The reduction, washing, drying and potassium acetate impregnation steps were the same for

both catalyst preparations.

With reference to Catalyst Y, the suffixes A, B and C in Table F denote different preparations ("lots") of nominally the same catalyst and, with respect to Catalysts Y and Z, the suffixes 1 and 2 denote duplicate analyses of different samples from the same lot of the catalysts.

Catalyst Z has a high palladium content and uses a cadmium co-catalyst rather than gold. Cadmium is significantly more toxic than gold. In addition, Catalyst Z is prepared by a process substantially different from the process of this invention, that is, Catalyst Z is prepared by impregnating a support with a solution of palladium, cadmium and potassium acetates and drying. There are no precipitation, reduction or washing steps in the process used to produce Catalyst Z.

TABLE F

	%Pd	%Au	%Cd	%K	%Na	STY
Catalyst X*	0.53	0.22	0	2.36	0.54	272
Model Catalyst	0.53	0.22	0	2.36	0.15	589
Catalyst YA-1*	0.49	0.19	0	2.29	0.60	360
Model Catalyst	0.49	0.19	0	2.29	0.15	546
Catalyst YA-2*	0.49	0.19	0	2.31	0.60	360
Model Catalyst	0.49	0.19	0	2.31	0.15	545
Catalyst YB*	0.63	0.24	0	2.27	0.70	386
Model Catalyst	0.63	0.24	0	2.27	0.15	669
Catalyst YC-1*	0.61	0.24	0	2.24	0.69	395
Model Catalyst	0.61	0.24	0	2.24	0.15	653
Catalyst YC-2*	0.61	0.26	0	2.18	0.70	395
Model Catalyst	0.61	0.26	0	2.18	0.15	658
Catalyst Z-1*	2.16	0	1.88	1.89	0.08	685
Model Catalyst	Outside range of models					
Catalyst Z-2*	2.16	0	1.89	1.92	0.09	685
Model Catalyst	Outside range of models					

*Comparative Catalysts

SUMMARY OF EMBODIMENT B OF THE INVENTION

Embodiment B of this invention is based, in part, on the discovery that the activity of alkenyl alkanoate catalyst produced by the process of U.S. Patent 4,048,096 is increased if, after above-described step (7) of the process of that patent, the sodium content of the catalyst is reduced by washing the catalyst with water or with an aqueous solution of a potassium promoter.

More specifically, Embodiment B of this invention provides a process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and a potassium promoter, said process comprising the steps of:

- impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;
- precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;
- converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent; and
- washing the impregnated support with water,
- drying the washed impregnated support,
- further impregnating the support particles with a potassium promoter,
- drying the support so impregnated to produce a dried catalyst containing sodium owing to the presence of sodium in one or more of the materials used in steps (a) to (f),
- washing the dried catalyst with water or with an aqueous solution containing a potassium promoter so as to reduce the amount of sodium in the catalyst and thereby to increase the activity of the catalyst,

and

(i) drying the catalyst.

In the practice of the process of Embodiment B of this invention, it is preferred to use an aqueous solution containing a potassium promoter in step (h) to avoid lowering the concentration of the potassium promoter [with which the support was impregnated in step (f)] below the desired level. Such undesirable lowering of promoter concentration may occur if water as such is used in step (h). However, if water is used in step (h) and the promoter concentration is thereby undesirably decreased, then step (i) can be followed by step (j) which is a second potassium promoter impregnation and then by step (k) which is a third drying. In some instances, excess potassium promoter can be used in the initial potassium promoter impregnation [step (f)] to ensure that the product of step (i) has the desired level of potassium promoter even after water washing [step (h)]. The latter procedure also obviates the need for steps (j) and (k).

Without wishing to be bound by any particular theory, it is believed that the potassium promoter used in the catalyst preparation procedure of Bissot displaces at least a portion of the sodium which was bound to ion-exchange sites on the catalyst support. The source of the sodium is the starting materials (especially the precipitating agent) used in the Bissot (U.S. Patent 4,048,096) catalyst preparation procedure. Although displaced by the potassium promoter, such sodium remains in the catalyst produced by the Bissot process as an activity-suppressing impurity. In the process of this invention, the displaced sodium is readily removed from the catalyst by merely washing the catalyst with water or with an aqueous solution containing a potassium promoter [step (h)]. Prior to its displacement by the potassium promoter in step (f), the sodium cannot be effectively removed from the catalyst by the simple water washing [i.e., as in step (d)] because the sodium is too tightly bound to the support. However, step (d) is effective in removing unbound impurities, particularly chlorides and excess reagents from steps (a) through (c).

BRIEF DESCRIPTION OF THE DRAWING ILLUSTRATING EMBODIMENT B

Figure 1 shows the predicted effect of sodium on the performance of vinyl acetate catalysts produced in accordance with Embodiment B of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF EMBODIMENT B

The support particles used in Embodiment B of the process of this invention are solid particulate materials that are capable of exchanging cations, that are capable of being impregnated with palladium, gold and a potassium promoter and that are inert under the conditions used to produce alkenyl alkanoates. Illustrative of such support particles are particulate silica, alumina, and silica-aluminas. Silica is the preferred support. The support preferably has a surface area from 100 to 800 square meters per gram.

The aqueous solutions of water-soluble palladium and gold compounds used in Embodiment B of the process of this invention include aqueous solutions of any suitable palladium or gold compound such as palladium (II) chloride, sodium tetrachloropalladium (II) (Na_2PdCl_4), palladium (II) nitrate, palladium (II) sulfate, gold (III) chloride or auric (III) acid (HAuCl_4). The volume of the solution preferably corresponds to from 95 to 100% (more preferably from 98 to 99%) of the pore volume of the support.

The precipitating agents used in Embodiment B of the process of the present invention catalysts include sodium, lithium and potassium silicates and hydroxides. The precipitating agents are preferably employed in the form of aqueous solutions containing a 1.6 to 1.8 molar excess of the precipitating agents. The volume of such solutions used is preferably just sufficient to cover the support particles.

The reducing agents used in Embodiment B of the process of this invention include hydrazine, ethylene, formaldehyde, hydrogen and sodium borohydride. The reducing agents are preferably employed in the form of aqueous solutions containing a 50:1 (or more preferably a 10:1) molar excess of the reducing agents. If hydrogen is used, it is usually necessary to heat the catalyst to 100 to 300 °C to complete the reduction.

The potassium promoters used in Embodiment B of the process of this invention for producing alkenyl alkanoate catalysts include potassium alkanoates and any potassium compound that is converted to a potassium alkanoate during the alkenyl alkanoate-forming reaction (i.e., the reaction of ethylene, an alkanoic acid and an oxygen-containing gas in the presence of the catalyst to produce a alkenyl alkanoate). Suitable potassium compounds include potassium acetate, bicarbonate, nitrate and (when a stable support is used) hydroxide. The promoters are preferably applied in the form of aqueous solutions.

Washing steps (d) and (h) of Embodiment B of the process of this invention can be conducted batchwise or continuously. Continuous washing is more efficient but may not be most suitable for large scale (e.g., plant scale) catalyst production. In continuous washing, the wash liquid is slowly and continu-

ously passed through the catalyst over a period of time (e.g., from 8 to 24 hours). In batch washing, the catalyst is contacted with the wash liquid, the mixture is allowed to stand (e.g., for from 0.5 to 2.0 hours) and the liquid and catalyst are separated. In batch washing, several such washes (e.g., from 2 to 10, or preferably from 4 to 6 washes) are often required. Temperatures from 20 °C to 80 °C and volume ratios of wash liquid to catalyst of from 2:1 to 100:1 can be used in either batch or continuous washing.

The washing of the catalyst with water or an aqueous solution containing a potassium promoter in step (h) of Embodiment B of the process of this invention is distinct from the potassium promoter impregnation steps of prior art processes for producing alkenyl alkanoate catalysts. Such prior art impregnation steps are conducted by the incipient wetness technique or the decantation technique. In the incipient wetness technique [see the Example 5 of British Patent 1,215,210 (National Distillers)], the catalyst is contacted with the minimum amount of aqueous potassium promoter solution required to fill the pores of the support and to impregnate the catalyst with the desired amount of potassium promoter. Then the water is evaporated. No sodium can be removed from the catalyst by that technique. In the decantation technique, the catalyst (preferably dry) is immersed in a larger volume of the aqueous potassium promoter solution than is used in the incipient wetness technique. After the pores are filled with the solution, the excess solution is decanted and the catalyst is dried. Only one immersion and decantation operation is conducted and the contact time is relatively short. Hence, only a minimal amount of sodium can be removed from the catalyst by the decantation technique. Example 9 of U.S. Patent 3,743,607 (Sennewald et al.) illustrates the decantation technique using a moist catalyst.

The drying of the catalyst in accordance with steps (e), (g), (i) or (k) of the Embodiment B process of this invention for producing alkenyl alkanoate catalysts can be conducted in any convenient manner. By way of illustration, drying can be conducted at 40 °C to 120 °C in a forced air oven for 15 to 30 hours.

EXAMPLES ILLUSTRATING EMBODIMENT B

In the following Examples illustrating Embodiment B, the abbreviations have the same meanings as the abbreviations defined above used in the Examples illustrating Embodiment A.

In the following Examples illustrating Embodiment B, the following procedures were used:

Catalyst Preparation Procedure

A. Support I (15 g) was added to a solution of Na₂PdCl₄ (35.86% Pd, 0.258 g) and HAuCl₄ (48.95% Au, 0.094 g) dissolved in 9.0 ml of deionized water. The mixture so formed was gently agitated until all of the moisture was absorbed into the support and then was allowed to stand in a sealed flask for about one hour at room temperature so as to impregnate the support with the palladium and gold salts. The damp catalyst was covered with a solution of either sodium hydroxide (0.236 g in 28 ml water) or sodium metasilicate, Na₂SiO₃, (0.837 g in 28 ml water) as a precipitating agent. After mixing for a few seconds, the mixture was allowed to stand covered and undisturbed for 23 hours at room temperature to deposit water-insoluble palladium and gold compounds on the support. The palladium and gold were then reduced by the addition of 1.0 g of 85% hydrazine hydrate to the above mixture. The mixture was agitated for a few seconds and allowed to stand covered and undisturbed at room temperature for another 23 hours. The supernatant liquid was decanted from the catalyst and the catalyst was rinsed four times with water to remove the small amount of metal sludge present. The catalyst was washed thoroughly by either the Column Washing Procedure or the Batch Washing Procedure described below. The catalyst was dried on a stainless steel screen at 60 °C in a forced air oven for 20 to 24 hours. The catalyst was analyzed for potassium using AA Analysis. Then the catalyst was impregnated with the desired amount of potassium acetate in water using the impregnation technique described above for the palladium and gold salts. Then the impregnated catalyst was dried at 60 °C for 20 to 24 hours. The prior art process of U.S. Patent 4,048,096 (Bissot) [i.e., above described steps (a) to (g)] is complete at this point. The process of Embodiment B of this invention has the additional steps (h) and (i) followed by, if desired, steps (j) and (k) as illustrated below.

B. The palladium, gold, sodium, and potassium contents in the finished catalysts were determined by ICP analyses. In most cases, sodium and potassium were also determined by AA Analyses for greater accuracy.

C. Unless otherwise noted, the foregoing procedure was used to prepare all the catalysts referred to in the following Examples. When different quantities of Support I were used, the quantities of the other starting materials used were varied correspondingly.

D. All the catalysts produced as described in the Examples appearing below were shell-impregnated (i.e., substantially all of the palladium and gold was present in a shell within 0.5mm of the surface of the beads of Support I.)

5 Catalyst Washing Procedures (same as for above Examples illustrating Embodiment A)

Catalyst Test Method (same as for above Examples illustrating Embodiment A)

EXAMPLE I

10

A. Comparative

An important step in alkenyl alkanoate catalyst preparation is the water washing step which is known to remove liberated chloride and residual starting materials. In the laboratory, catalysts are conveniently washed in a column over a 20 to 24-hour period, using about 60-80 ml of water per gram of catalyst. For
15 practical and economic reasons, large-scale (e.g., pilot plant) preparations are washed batchwise over a much shorter time using significantly lower volumes of water per volume of catalyst washed. Catalysts made in large-scale equipment have been found to be less active than catalysts made in laboratory scale equipment. It was suspected that the activity differences were due to less efficient washing in the large-
20 scale equipment.

Table I compares typical performance results of laboratory prepared catalysts with catalysts prepared in large-scale equipment following the process of U.S. Patent 4,048,096 (Bissot). Specifically, all the catalysts were made using the Catalyst Preparation Procedure with sodium metasilicate as the precipitating agent, except that the amounts of starting material was scaled up in the large-scale preparations and except for the
25 differences in washing procedures. In the laboratory-scale preparations, the Column Washing Procedure was used and, in the large-scale preparations, the Batch Washing Procedure was used. The catalysts prepared using large-scale equipment include 80-liter pilot plant samples as well as samples from 260-liter equipment typical of that intended for full commercial production. The catalysts prepared using the large scale equipment typically contained about 5 to 10 weight percent more palladium than the catalysts
30 prepared in the laboratory, yet the STY's of catalysts prepared in large-scale equipment are about 5 to 10 percent lower.

35

40

45

50

55

TABLE I

Activities of Laboratory-Scale And Large-Scale Catalysts Preparations

Catalyst of Comparative Example	STY(a)	Spec. Act.(b)	%Pd(c)	%Au(c)
<u>Laboratory-Scale Preparations</u>				
I-1	571(3)	197.0	0.516	0.198
I-2	546(3)	188.5	0.516	0.208
I-3	543	191.6	0.505	0.198
I-4	556(2)	181.9	0.510	0.200
I-5	547	194.4	0.500	0.190
I-6	567	198.0	0.510	0.200
Average	555	191.9		
<u>Large-Scale Preparations</u>				
I-7(d)	521	165.4	0.558	0.231
I-8(d)	532(2)	172.0	0.554	0.248
I-9(d)	534(2)	172.7	0.553	0.238
I-10(d)	521(2)	168.5	0.552	0.237
I-11(e)	495(6)	163.0	0.543	0.214
I-12(e)	484	156.5	0.553	0.223
I-13(e)	485	156.9	0.554	0.222
I-14(e)	528	173.9	0.589	0.226
I-15(e)	525	172.8	0.568	0.217
I-16(e)	468	154.1	0.536	0.204
I-17(e)	489(2)	155.5	0.562	0.213
I-18(e)	520	165.1	0.564	0.212
I-19(e)	479	149.6	0.568	0.203
Average	497	160.6		

(a) STY = Space Time Yield, g VA/l cat/hr, value in parentheses is the number of runs averaged; (b) Specific Activity, g VA/g Pd/hr; (c) Wt % Pd and Au as determined by ICP analyses; (d) 80-liter pilot plant run; (e) 260-liter plant-scale run.

B. Embodiment B of Present Invention

The data in Table I shows that the catalysts made on a large scale had lower activities than the catalysts made on a laboratory scale. To determine whether insufficient washing accounted for the lower activity of the catalysts made on a large scale, four of the catalysts made in large scale equipment (i.e., I-7,

I-9, I-12 and I-17 of Table I) were rewashed (step (h) of the process of this invention) with water using the Column Washing Procedure and then dried [step (i) Embodiment B of the process of this invention]. A fifth catalyst was prepared on a laboratory scale using the Catalyst Preparation Procedure and the Batch Washing Procedure and a portion of this catalyst was rewashed with water (step (h) of Embodiment B of the process of this invention) using the Column Washing Procedure and then dried [step (i) of Embodiment B of the process of this invention]. Each of the five rewashed and redried catalysts was reimpregnated (step (j) of Embodiment B of the process of this invention) with 5% potassium acetate to replace the potassium acetate assumed to have been removed during the rewashing and dried again [step (k) of Embodiment B of the process of this invention]. The results are shown in Table II and indicate that in every instance rewashing improved activity by 5 to 10 percent.

TABLE II

Effect of Rewashing on Catalyst Activity

<u>No.</u>	<u>Catalyst</u>	<u>Rewashed</u>	<u>STY</u>	<u>% Change</u>
<u>Large Scale Preparations</u>				
1*	I-7	No	521	-
2	I-7	Yes	557	+7
3*	I-9	No	534(2)	-
4	I-9	Yes	566	+6
5*	I-12	No	484	-
6	I-12	Yes	537	+11
7*	I-17	No	489(2)	-
8	I-17	Yes	524	+5
<u>Laboratory Preparation</u>				
9*		No	508	-
10		Yes	561	+10
* Comparative Examples				

EXAMPLE II

In the experiments described in Example I, it had been assumed that the rewashing (step (h) of the process of this invention) had also removed all the potassium acetate. Hence, in those experiments, potassium acetate had been reapplied (step (j) of the process of this invention) after the rewash in an amount equal to that used in the initial impregnation of the catalysts. The assumption made in connection with Example I was checked with another series of eight catalysts having varying potassium loadings. Analytical results obtained before and after rewashing are shown in Table III for these eight catalysts (Catalysts II-1 to II-8). These analytical results show that rewashing as described in Example I above did not, in fact, remove all the potassium acetate. The results shown in Table III indicate that about 0.9 weight percent potassium consistently remained in the catalyst after rewashing. It is believed that the potassium is bound to the support by an ion exchange mechanism.

TABLE III

Rewashing vs KOAc Removal			
Catalyst	Wt% K		Difference
	Original	Rewashed(a)	
II-1	2.80	3.67	0.86
II-2	1.50	2.33	0.83
II-3	1.40	2.27	0.87
II-4	1.40	2.35	0.95
II-5	2.70	3.51	0.81
II-6	1.40	2.35	0.95
II-7	2.90	3.64	0.73
II-8	2.80	3.68	0.87
			Average 0.86
			%RSD(b) 8.30

a) After reimpregnation with the same wt % KOAc as was present in the original catalyst.

b) RSD is the Relative Standard Deviation.

EXAMPLE III

In view of the findings shown in Table III, two of the rewashed catalysts shown in Table II were analyzed before reapplication of potassium acetate. Results, shown below, were generally consistent with those in Table III.

Rewashed Catalyst	% K Retained
I-12	0.88
I-17	1.19

As a consequence, the potassium loadings of all the rewashed catalysts reported in Table II were probably about 0.8 to 1.2% higher than anticipated. The higher than the desired potassium levels would be expected to decrease catalyst activity. This data suggests that activity improvements even greater than the observed 5-10% shown in Table II would be possible with proper (lower) final potassium loadings. This was confirmed when the amount of potassium added after rewashing was only the amount required to achieve the original loading as shown by Runs III-1 to III-7 below.

Comparative Run III-1: A 2.5 g portion of Catalyst II was evaluated for vinyl acetate production giving the result reported in Table IV. Portions of this catalyst were rewashed as described in Runs III-2 and III-3 below.

Run III-2: Three 50-g portions of catalyst from Run III-1 were each washed using the Column Washing Procedure and then analyzed for potassium which gave a potassium value of 0.92 wt. %. A 15-g sample of the catalyst was reimpregnated with 0.469 g of potassium acetate in 9.0 ml of water, then dried 18 hrs at 60 °C. The analysis and test results for the catalyst are provided in Table IV.

Run III-3: The procedure of Run III-2 above was used, except that four samples of Catalyst II were used and each portion (200g) was washed with 2 gallons of water over a 48-hr period using the Column Washing Procedure. The potassium level was determined to be 0.86% after combining the washed material. A 15 g sample was impregnated with a solution of 0.556 g of potassium acetate in 9.0 ml of water then dried for 24 hrs at 60 °C. The analysis and test results on the catalyst are shown in Table IV.

Comparative Run III-4: This catalyst was prepared using the Catalyst Preparation Procedure, except that the concentrations of the palladium and gold salts in the impregnation solution and the other starting materials were adjusted to give the loadings shown in Table IV. Evaluation was done using the Catalyst Test Method, except that only 0.75 grams of catalyst were used. The analysis and test results are shown in Table IV.

Run III-5: A 2.75 g portion of the catalyst from Run III-4 was washed using the Column Washing Procedure using 500 ml of water over 24 hours. After drying, the catalyst was impregnated with sufficient potassium acetate to give about 3% potassium in the finished catalyst. Evaluation was done using the Catalyst Test Method, except that only 0.75 grams of catalyst were used. The analysis and test results are shown in Table IV.

Comparative Run III-6: This catalyst was prepared as per Run III-4 above, except that the concentrations of the palladium and gold salts in the impregnation solution and the other starting materials were adjusted to give the loadings shown in Table IV. Evaluation was done using the Catalyst Test Method, except that only 0.75 grams of catalyst were used. The analysis and test results on the catalyst are provided in Table IV.

Run III-7: A sample of catalyst from Run III-6 was rewashed with water using the Column Washing Procedure. Evaluation was done using the Catalyst Test Method described above, except that only 0.75 grams of catalyst were used. The analysis and test results on the catalyst are provided in Table IV.

TABLE IV

Effect of Rewashing at Constant Potassium Loading(a)							
Run	%Pd	%Au	%KOAc	% Na	Rewashed	STY	% Change
III-1*	0.55	0.22	5.8	0.45	No	565	---
III-2	0.55	0.22	5.3	0.14	Yes	615	+9
III-3	0.5	0.22	5.8	0.12	Yes	642	+14
III-4*	0.56	0.46	7.6	0.42	No	734(b)	---
III-5	0.56	0.46	7.6	0.17	Yes	850(b)	+15
III-6*	1.02	0.46	7.2	0.48	No	967(b)	---
III-7	1.02	0.47	7.7	0.17	Yes	1141(b)	+18

(a) The Column Washing Procedure was used both in the original preparations and in rewashing.

(b) This catalyst was tested at low conversion which accounts for the exceptionally high STY observed for this metal loading.

* Comparative Examples.

On the basis of the results described above, studies were conducted to determine if other impurities might account for the described effects. Comparison of ICP analytical data from the original catalysts and their rewashed versions revealed significant differences in sodium content but no significant differences in other impurities were observed.

EXAMPLE IV

To test the effect of sodium on catalyst activity, a series of experiments (runs) were conducted where sodium was varied and the potassium level was held constant. In another series of experiments (runs) the sodium to potassium ratio was varied while keeping the total moles of alkali constant. The results of both series of experiments are shown in Table V and the results confirm that increasing levels of sodium do, in fact, result in diminished activity.

In Run 2 of Table V, a rewashed catalyst which was impregnated with a level of sodium similar to that in the original unwashed version (Run 4 of Table V) showed an appreciably higher activity. This suggests that another detrimental impurity may also be removed by rewashing.

TABLE VEffect of Sodium on Catalyst Performance

Run No.	% K	% Na	STY	% Selectivity
<u>Constant K content & varied Na content (a)</u>				
1	2.24	0.117	642	93.1
2	2.22	0.457	609	93.5
3	2.18	0.912	540	94.1
4	2.31	0.453	563	93.4
<u>Varied Na/K at constant moles alkali(b)</u>				
1	2.21	0.435	616	93.6
2	1.77	0.705	584	94.0
3	0.77	1.300	501	94.2
(a) Column rewashed Catalyst II was reimpregnated with KOAc and NaOAc solutions.				
(b) Prepared by appropriate addition of KOAc and NaOAc to subsamples of a master batch of Catalyst I.				

SUMMARY OF EMBODIMENT C OF THE INVENTION

Embodiment C of this invention is based, in part, on the discovery that the activity of alkenyl alkanoate catalysts is increased if the sodium content thereof is decreased by washing the catalysts, at a particular intermediate point in their production, with a cation exchange solution.

More specifically, Embodiment C of this invention provides a process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate, said process comprising the steps of:

(a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;

(b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;

(c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent so as to produce an impregnated support containing sodium owing to the presence of sodium in one or more of the materials used in steps (a) to (c);

(d) washing the impregnated support particles with a cation exchange solution so that the amount of sodium in the catalyst is reduced and the activity of the catalyst is increased; and

(e) drying the washed and impregnated support particles to produce the catalyst.

If it is desired to increase further the activity of the catalyst produced by Embodiment C of the process of this invention, the above steps can be followed by the steps of:

(f) impregnating the dried support particles with a potassium promoter; and

(g) drying the catalyst (see Run I-2A below and Figure 1).

However, such further increase in the activity of the catalyst is preferably achieved as described below in connection with the preferred embodiment of this invention which involves the use of particular concentra-

tions and amounts of particular cation exchange solutions (i.e. potassium promoter solutions) for that purpose (see also Examples VII to XII below and Figure 3).

Embodiment C of this invention also provides alkenyl alkanoate catalysts having reduced sodium contents and a process for producing alkenyl alkanoates using such catalysts.

Without wishing to be bound by any particular theory, it is believed that sodium impurities in alkenyl alkanoate catalysts reduce the activity of the catalysts and that the cations in the cation exchange solutions used in step (d) of Embodiment C of the process of the present invention displace sodium (and perhaps other ion-exchangeable impurities) from the supports so that the impurities can be washed from the supports in step (d). As a result of the reduction in sodium content, the activity of the catalysts is increased.

BRIEF DESCRIPTION OF THE DRAWINGS ILLUSTRATING EMBODIMENT C

Figure 1 shows the predicted effect of sodium on the performance of vinyl acetate catalysts produced in accordance with this invention.

Figure 2 shows various batch-washing experiments in accordance with Embodiment C of this invention.

Figure 3 shows the vinyl acetate catalyst preparation procedure of U.S. Patent 4,048,096 and the catalyst preparation procedure of the preferred embodiment of Embodiment C of this invention.

Figure 4 shows the effect of the washing procedure on catalyst activity in accordance with Embodiment C of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF EMBODIMENT C

PROCESS FOR PRODUCING CATALYSTS

The cation exchanged solutions employed in Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts are solutions which contain a cation that exchanges with sodium on the support and which does not impair, and preferably promotes, the activity of the catalyst. Suitable cation exchange solutions include, but are not limited to, solutions of potassium promoters. Preferred cation exchange solutions are aqueous solutions containing from 0.01 to 20 weight percent of a compound containing a suitable cation. Such compounds include, but are not limited to, potassium acetate, lithium acetate, potassium nitrate, potassium carbonate, ammonium carbonate, ammonium acetate, and magnesium acetate. More preferred are solutions containing from 0.1 to 10 weight percent (and most preferred from 0.5 to 7 weight percent) of the compound containing a suitable cation.

In order to economize on the amount of the compound containing the cation in the cation exchange solutions used in Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts, the washing with the cation exchange solution can be preceded by one or more washes with water to remove impurities that are not strongly associated with the support (e.g., chlorides and unbound sodium).

The optimum concentration of the ion exchange solution used in Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts will depend on factors such as the sodium content in the catalyst, the volume of wash solution employed, the total washing time, etc. and is best determined by experimentation. Concentrations of the compound containing a suitable cation of about 10% or higher are less preferred because they are wasteful of the compounds and sometimes give catalysts having lower activities.

The potassium promoters used in step (d) or in step (f) of Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts include potassium alkanoates and any potassium compound that is converted to a potassium alkanoate during the alkenyl alkanoate-forming reaction (i.e., the reaction of an alkene, an alkanolic acid and an oxygen-containing gas in the presence of the catalyst to produce an alkenyl alkanoate). Suitable potassium compounds include potassium acetate, bicarbonate, nitrate and (when a stable support is used) hydroxide. The promoters are preferably used in the form of aqueous solutions.

When the cation in the cation exchange solution used in step (d) in Embodiment C of the process of the present invention for producing alkenyl alkanoate catalysts is potassium, potassium is thereby introduced into the catalyst. In such cases, the catalyst should be dried and analyzed for potassium to determine how much more potassium should be added in step (f). This procedure is necessary to avoid producing a catalyst having an excess or a deficiency of potassium, either of which can cause a decrease in catalyst activity.

The preferred embodiment of Embodiment C of the process of the present invention for producing alkenyl alkanoate catalysts involves using a solution of the potassium promoter as the cation exchange

solution in step (d) and employing a sufficient concentration and amount of the potassium promoter solution in that step so that the potassium acetate impregnation step [step (f)] and the second drying step [step (g)] are not required. This embodiment is illustrated in Figure 3.

More specifically, the preferred embodiment of Embodiment C of the process of the present invention for producing alkenyl alkanoate catalysts comprises the steps of:

- (a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;
- (b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;
- (c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent, said impregnated support containing sodium owing to the presence of sodium in one or more of the materials used in steps (a) to (c);
- (d) washing the support particles with a potassium promoter solution in a concentration and in an amount sufficient both: (I) to reduce the amount of sodium in the catalyst so as to increase the activity of the catalyst and (II) to further impregnate the catalyst with the amount of potassium necessary to further promote the activity of the catalyst; and
- (e) drying the washed and further impregnated support particles to produce the catalyst.

The appropriate potassium promoter concentration in the cation exchange solution used in the washing step (d) of the preferred embodiment of Embodiment C of this invention will depend upon such factors as the ion exchange properties of the support material and its pore volume and the desired activity of the catalyst. For this reason, the optimum concentration is best determined by routine experimentation. A five percent aqueous potassium acetate solution has been found to give good results.

When using the catalyst preparation process described in U. S. Patent 4,048,096 (Bissot), some colloidal palladium and gold are washed from the catalyst support during the washing step. Another benefit of the practice of the present invention is a more efficient utilization of metals during catalyst preparation when a potassium acetate solution is used as the cation exchange solution. Surprisingly, no detectable amount of palladium or gold is removed from the catalyst support when the potassium acetate solution is employed as the cation exchange solution in the practice of the present invention. Examples I-1A and I-2A below show that one weight percent of the palladium and gold were washed from the catalyst using the Bissot process but no detectable amounts of these metals were washed out in the process of this invention. This benefit not only results in improved efficiency of metal deposition but also serves to reduce the cost of recovery of the precious metals from the washings.

The support particles used in Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts are solid particulate materials that are capable of exchanging cations, that are capable of being impregnated with palladium, gold and a potassium promoter and that are inert under the conditions used to produce alkenyl alkanoates. Illustrative of such support particles are particulate silica, alumina, and silica-aluminas. Silica is the preferred support. The support preferably has a surface area from 100 to 800 square meters per gram.

The aqueous solutions of water-soluble palladium and gold compounds used in Embodiment C of the process of this invention for making alkenyl alkanoate catalysts include aqueous solutions of any suitable palladium or gold compound such as palladium (II) chloride, sodium tetrachloropalladium (II) (Na_2PdCl_4), palladium (II) nitrate, palladium (II) sulfate, gold (III) chloride or auric (III) acid (HAuCl_4). The volume of the solution preferably corresponds to from 95 to 100% (more preferably from 98 to 99%) of the pore volume of the support.

The precipitating agents used in Embodiment C of the process of the present invention for producing alkenyl alkanoate catalysts include sodium, lithium and potassium silicates and hydroxides. The precipitating agents are preferably employed in the form of an aqueous solutions containing a 1.6 to 1.8 molar excess of the precipitating agents. The volume of such solutions used is preferably just sufficient to cover the support particles.

The reducing agents used in Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts include hydrazine, ethylene, formaldehyde, hydrogen and sodium borohydride. The reducing agents are preferably employed in the form of an aqueous solutions containing a 50:1 (or more preferably a 10:1) molar excess of the reducing agents. If hydrogen is used, it is usually necessary to heat the catalyst to 100° to 300° C to complete the reduction.

The washing step [step (d)] used in Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts can be conducted batchwise or continuously. Continuous washing is more efficient but may not be most suitable for large scale (e.g., plant scale) catalyst production. In continuous washing, the cation exchange solution is slowly and continuously passed through the catalyst over a period

of time (e.g. for from 8 to 24 hours). In batch washing, the catalyst is contacted with the cation exchange solution, the mixture is allowed to stand (e.g., for from 0.5 to 2.0 hours) and the solution and catalyst are separated. In batch washing, several such washes (e.g., from 2 to 10, or preferably from 4 to 6 washes) are often required to reduce the sodium content of the catalyst to the desired level. Temperatures from 20 °C to 80 °C and ratios of cation exchange solution to catalyst of from 2:1 to 100:1 can be used in either batch or continuous washing.

The washing of the catalyst with a cation exchange solution in accordance with step (d) of Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts is distinct from the potassium promoter impregnation steps of prior art processes for producing alkenyl alkanoate catalysts. Such prior art impregnation steps are conducted by the incipient wetness technique or the decantation technique. In the incipient wetness technique [see the Example 5 of British Patent 1,215,210 (National Distillers)], the catalyst is contacted with the minimum amount of aqueous potassium promoter solution required to fill the pores of the support and to impregnate the catalyst with the desired amount of potassium promoter. Then the water is evaporated. No sodium can be removed from the catalyst by that technique. In the decantation technique, the (preferably dry) catalyst is immersed in a larger volume of the aqueous potassium promoter solution than is used in the incipient wetness technique. After the pores are filled with the solution, the excess solution is decanted and the catalyst is dried. Only one immersion and decantation operation is conducted and the contact time is relatively short. Hence, only a minimal amount of sodium can be removed from the catalyst by the decantation technique. Example 9 of U.S. Patent 3,743,607 (Sennewald et al.) illustrates the decantation technique using a moist catalyst.

The drying of the catalyst in accordance with step (e) of Embodiment C of the process of this invention for producing alkenyl alkanoate catalysts can be conducted in any convenient manner. By way of illustration, drying can be conducted at 40 °C to 120 °C in a forced air oven for 15 to 30 hours.

25 EXAMPLES ILLUSTRATING EMBODIMENT C

In the following Examples illustrating Embodiment C, the abbreviations used have the same meaning as set out above for the Examples illustrating Embodiment A.

In the following Examples, the following procedures were used:

30 Catalyst Preparation Procedure

A. Support I (15 g) was added to a solution of Na_2PdCl_4 (35.86% Pd, 0.258 g) and HAuCl_4 (48.95% Au, 0.094 g) dissolved in 9.0 ml of deionized water. The mixture so formed was gently agitated until all of the moisture was absorbed into the support and then was allowed to stand in a sealed flask for about one hour at room temperature so as to impregnate the support with the palladium and gold salts. The damp catalyst was covered with a solution of either sodium hydroxide (0.236 g in 28 ml water) or sodium metasilicate, Na_2SiO_3 , (0.837 g in 28 ml water) as a precipitating agent. After mixing for a few seconds, the mixture was allowed to stand covered and undisturbed for 23 hours at room temperature to deposit water-insoluble palladium and gold compounds on the support. The palladium and gold were then reduced by the addition of 1.0 g of 85% hydrazine hydrate to the above mixture. The mixture was agitated for a few seconds and allowed to stand covered and undisturbed at room temperature for another 23 hours. The supernatant liquid was decanted from the catalyst and the catalyst was rinsed four times with water to remove the small amount of metal sludge present. The catalyst was washed thoroughly by either the Column Washing Procedure or the Batch Washing Procedure described below. The catalyst was dried on a stainless steel screen at 60 °C in a forced air oven for 20 to 24 hours. In practice the preferred embodiment of Embodiment C of this invention, the Catalyst Preparation Procedure was complete at this point.

B. In the practice of other embodiments of Embodiment C of this invention and in the practice of the prior art procedures and comparative Examples described below, the Catalyst Preparation Procedure also involved the following additional steps: The catalyst was analyzed for potassium using AA Analysis. Then the catalyst was impregnated with the desired amount of potassium acetate in water using the impregnation technique described above for the palladium and gold salts. The impregnated catalyst was then dried at 60 °C for 20 to 24 hours.

C. The palladium, gold, sodium, and potassium contents in the finished catalysts were determined by ICP analyses. In most cases, sodium and potassium were also determined by AA Analyses for greater accuracy.

D. Unless otherwise noted, the foregoing procedure was used to prepare all the catalysts referred to in the following Examples. When different quantities of support were used, the quantities of the other starting materials used were varied correspondingly.

E. All the catalysts produced as described in the Examples appearing below were shell impregnated (i.e., substantially all of the palladium and gold was present in a shell within 0.5 mm of the surface of the beads of Support I).

The Catalyst Washing Procedures and the Catalyst Test Method were the same as those used in the above Examples illustrating Embodiment A.

EXAMPLE I

Comparative Run I-1A: A 90 g. sample of Support I was impregnated as described in the Catalyst Preparation Procedure using sodium metasilicate as the precipitating agent. After the reduction step, the supernatant liquid was decanted, and the wet beads were divided into three equal portions labeled Samples A, B and C. Samples B and C were retained for later use. Sample A was transferred without drying to the washing apparatus and washed with water using the Column Washing Procedure. The cloudy black washings taken from the column were analyzed by ICP for palladium and gold. The results indicated about 1% of each metal was lost from the catalyst during washing. The catalyst was dried at 60 °C in a forced-air oven for 4.5 hrs. then analyzed for potassium (0.31 wt%). The catalyst (30.4 g) was impregnated with a solution of 1.62 g of potassium acetate in 18.3 ml of water using the procedure described above under Catalyst Preparation Procedure. After drying at 60 °C for 24 hrs. the catalyst was tested for activity. The results are shown in Figure 1.

Run I-1B: A portion of the catalyst produced from Sample A described in Run I-1A above was rewashed with water using the Column Washing Procedure and dried. Then an amount of potassium acetate was added to increase the potassium acetate content back to its initial level. The results are shown in Figure 1.

Run I-2A: Sample B of the still-wet catalyst prepared in Run I-1A above, was washed using the Column Washing Procedure as above with the exception that 1% potassium acetate solution (a cation exchange solution) rather than water was used. The washings were colorless and showed no detectable palladium or gold by ICP. The washed catalyst was dried as above and analyzed for potassium (1.41%). The catalyst was impregnated with a solution of 0.608 g of potassium acetate in 17.8 ml of water then dried at 60 °C for 24 hrs. Test results are provided in Figure 1.

Run I-2B: A portion of the catalyst from Run I-2A above was rewashed with water using the Column Washing Procedure and dried. Then an amount of potassium acetate was added to increase the potassium acetate content back to its initial level. The results are shown in Figure 1.

Run I-3: Sample C from Run I-1A above was treated identically to Sample B of Run I-2A above, except 1% potassium hydroxide was substituted for the 1% potassium acetate solution in the washing step. After standing for about 12 hours, it was discovered that the silica support had badly degraded and the catalyst had to be discarded. This experiment shows that, under the conditions used, potassium hydroxide is not suitable for use as a cation exchange solution in the present invention when supports sensitive to strong base are used.

The results in Figure 1 show that the same activity improvement is obtained by initially using a potassium acetate wash or by using an initial water wash and then rewashing with water after potassium acetate impregnation. These results indicate the presence of a detrimental impurity on the catalyst and support the theory that potassium addition aided in the removal of that impurity.

EXAMPLE II

It was conceivable that chloride was, at least in part, the impurity removed by the experiments described in the above Example I. However, subsequent chloride analyses performed on the catalysts made in Example I (see Figure 4) indicated only minor differences in chlorine content before and after rewashing. Additional experiments in which varying levels of potassium chloride were added to catalysts also showed a minimal effect on activity (see Table G).

TABLE G

Effect Of Added Chloride		
Chloride (ppm)	STY	% Selectivity
0	605	93.7
50	601	93.7
100	598	93.5

The catalysts used to obtain the results shown in Table G were prepared using the Catalyst Preparation Procedure from the same master batch which had a nominal palladium loading of 0.58%, a Au/Pd ratio of 0.5, a KOAc loading of 5.3%, and an estimated initial chloride content of about 200 ppm. Chloride was added as KCl in the KOAc impregnation solution.

On the basis of the results described above, studies were conducted to determine if other impurities might account for the described effects. Comparison of ICP analytical data from the original catalysts and their rewashed versions revealed significant differences in sodium content but no significant differences in other impurities were observed.

EXAMPLE III

To test the effect of sodium on catalyst activity, a series of experiments (runs) were conducted where sodium was varied and the potassium level was held constant. In another series of experiments (runs) the sodium to potassium ratio was varied while keeping the total moles of alkali constant. The results of both series of experiments are shown in Table H and the results confirm that increasing levels of sodium do, in fact, result in diminished activity.

In Run 2 of Table H, a rewashed catalyst which was impregnated with a level of sodium similar to that in the original unwashed version (Run 4 of Table H below) showed an appreciably higher activity. This suggests that another detrimental impurity may also be removed by rewashing.

TABLE H

Effect of Sodium on Catalyst Performance

Run No.	% K	% Na	STY	% Selectivity
<u>Constant K content & varied Na content (a)</u>				
1	2.24	0.117	642	93.1
2	2.22	0.457	609	93.5
3	2.18	0.912	540	94.1
4	2.31	0.453	563	93.4
<u>Varied Na/K at constant moles alkali(b)</u>				
1	2.21	0.435	616	93.6
2	1.77	0.705	584	94.0
3	0.77	1.300	501	94.2
(a) Column rewashed Catalyst II was reimpregnated with KOAc and NaOAc solutions.				
(b) Prepared by appropriate addition of KOAc and NaOAc to subsamples of a master batch of Catalyst I.				

Example IV

A series of experiments (Runs IV-1 to IV-4 below) were conducted to further illustrate the effects shown in Example I above. An additional objective was to demonstrate that the benefits of this invention can also be obtained using the Batch Washing Procedure which is more amenable to large-scale catalyst preparation than the Column Washing Procedure which had been used in Example I above.

Comparative Run IV-1: A catalyst was prepared with 80 grams of Support I using the Catalyst Preparation Procedure. Sodium hydroxide was used as the precipitating agent. Following the reduction step, the liquid was drained from the catalyst beads and then the beads were rinsed quickly with a volume of water roughly equal to the catalyst volume. The catalyst was divided into four equal parts labelled Samples A, B, C, & D. Samples B, C and D were retained for use in the Examples which follow. Sample A was washed using the Batch Washing Procedure which involved covering the catalyst with 23 ml of deionized water and allowing it to stand for 36 minutes. The water was decanted and the catalyst covered with another 23 ml of fresh water. Washing was continued in this manner for a total of 5 washes done over a total of 3 hours. After the final wash, the beads were rinsed once with water then dried overnight at 60°C. The catalyst was analyzed for potassium (0.30%) and then impregnated with a solution of 0.955 g of potassium acetate in 11.7 ml of water. After drying at 60°C overnight catalyst evaluation gave the results provided in Table I.

Run IV-2: Sample B from Run IV-1 above was washed batchwise a total of five times over three hours with 23 ml quantities of 5% aqueous potassium acetate solution using the same procedure as that specified in Run IV-1 above. After rinsing the beads with water the catalyst was dried overnight at 60°C then analyzed for potassium (1.42%). The catalyst was then impregnated with a solution of 0.359 g of potassium acetate in 11.7 ml of water. After drying at 60°C overnight catalyst evaluation gave the results provided in Table I.

Comparative Run IV-3: Sample C from Run IV-1 above was washed five times with water in a manner identical to Run IV-1, above, except the duration of each wash was 96 minutes for a total of 8 hours washing time. Analysis for potassium showed 0.33% following washing. The sample was impregnated with a solution of 0.934 g of potassium acetate in 11.7 ml of water then dried overnight at 60 °C. Test results are provided in Table I.

Run IV-4 Sample D from Run IV-1 above was washed five times with 5% potassium acetate solution using the procedure of Run IV-3 above. Analysis for potassium showed 1.69% following washing. The sample was impregnated with a solution of 0.216 g of potassium acetate in 11.7 ml of water then dried overnight at 60 °C. Test results are provided in Table I.

Table I

Effect of Potassium Acetate Batch Washing on Performance			
Run	% K	% Na	STY
IV-1*	2.2	0.47	512
IV-2	2.4	0.22	531
IV-3*	2.1	0.47	535
IV-4	2.2	0.19	573

*Comparative Example

Example V

A further set of experiments was conducted to determine the most cost-effective quantity of potassium acetate required to give a significant activity improvement. In these experiments, a large batch of catalyst was divided just prior to the washing step (i.e., step (d) of the process of this invention) into six equal portions as shown in Figure 2. All catalysts were batch washed a total of five times using the Batch Washing Procedure. The compositions of the washing solutions were varied as indicated in Figure 2. For example, the first catalyst portion was batch washed five times with water; the second portion was washed three times with water followed by two times with 5% potassium acetate solution, etc. The catalysts were dried and analyzed by Atomic Absorption Spectroscopy for potassium and sodium. Each catalyst was again subdivided into "A" and "B" fractions. Each fraction was then treated with sufficient potassium acetate to bring the potassium level to about 2.9% in the finished catalyst. Those catalyst fractions labeled "B" also received sufficient sodium acetate to return their final sodium levels back to about the same level found in the water-washed catalyst (e.g., the level in the water-washed catalyst of Run V-1 below).

Thus two sets of catalysts were obtained: one set (the "A" series) shows the effect of potassium acetate washing on catalyst performance; and the second set (the "B" series) shows that sodium removal adequately accounted for that effect. These results are summarized in Table J.

Comparative Run V-1: A catalyst was prepared using the Catalyst Preparation Procedure with 100 grams of Support I and sodium metasilicate. After the reduction step, the solution was decanted and the catalyst was rinsed four times with water. The solutions of the precipitating agent and reducing agent were drained and the still-damp catalyst was divided into six equal portions, labeled Samples A, B, C, D, E, and F. Samples B through F were retained for use in the following Examples. Sample A was batch washed five times with about 20 ml quantities of water for a total of 8 hours. After drying overnight at 60 °C, the catalyst was impregnated with a solution of 1.098 g of potassium acetate in 9.6 ml of water and dried at 60 °C. The finished catalyst, which had the calculated potassium and sodium content shown in Table J, was evaluated for vinyl acetate activity. The results are shown in Table J.

Run V-2: Sample B from Run V-1 above was batch washed in a manner identical to that Run, except the first three washes consisted of water and the last two consisted of 5% potassium acetate solution. After drying overnight at 60 °C, the catalyst was divided equally. The first portion was impregnated with 0.26 g of potassium acetate in 4.6 ml of water. After drying at 60 °C the catalyst, which had the calculated composition provided in Table J (Run V-2A), gave the results provided in the same table. The second half of the sample was impregnated with a solution of 0.26 g of potassium acetate and 0.090 g of sodium acetate in 4.6 ml of water. The calculated composition and results are shown in Table J (Run V-2B).

Run V-3: Sample C from Run V-1 above was batch washed in a manner identical to that Run, except the first two washes consisted of water and the last three consisted of 5% potassium acetate solution. After

drying overnight at 60 °C, the catalyst was divided equally. The first portion was impregnated with 0.20 g of potassium acetate in 4.6 ml of water. After drying the catalyst, which had the calculated composition shown in Table J (Run V-3A), gave the results provided in the same table. The second half of the sample was impregnated with a solution of 0.20 g of potassium acetate and 0.097 g of sodium acetate in 4.6 ml of water. The calculated composition and test results are given in Table J (Run V-3B).

Run V-4: Sample D from Run V-1 above was batch washed in a manner identical to Run V-1 above, except that the first wash consisted of water and the last four consisted of 5% potassium acetate solution. After drying overnight at 60 °C, the catalyst was divided equally. The first portion was impregnated with 0.155 g of potassium acetate in 4.6 ml of water. After drying the catalyst, which had the calculated composition provided in Table J (Run V-4A), gave the results provided in the same table. The second half of the sample was impregnated with a solution of 0.155 g of potassium acetate and 0.094 g of sodium acetate in 4.6 ml of water. The calculated composition after drying and test results are shown in Table J (Run V-4B).

Run V-5: Sample E from Run V-1 above was batch washed in a manner identical to Run V-1 above, except that the first three washes consisted of water and the last two consisted of 10% potassium acetate solution. After drying overnight at 60 °C, the catalyst was divided equally. The first portion was impregnated with 0.032 g of potassium acetate in 4.6 ml of water. After drying the catalyst, which had the calculated composition provided in Table J (Run V-5A), gave the results provided in the same table. The second half of the sample was impregnated with a solution of 0.032 g of potassium acetate and 0.098 g of sodium acetate in 4.6 ml of water. The calculated composition after drying and test results are shown in Table J (Run V-5B).

Run V-6: Sample F from V-1 above was batch washed in a manner identical to V-1 above, except that the first two washes consisted of water and the last three consisted of 10% potassium acetate solution. After drying overnight at 60 °C, the catalyst was divided equally. The first portion was dried and divided without further impregnation with potassium acetate. The catalyst, which had the calculated composition provided in Table J (Run V-6A) gave the results provided in the same table. The second half of the sample was impregnated with a solution of 0.12 g of sodium acetate in 4.6 ml of water. The calculated composition after drying and test results are shown in Table J below (Run V-6B).

TABLE J

Batch-Washing Studies

Run No.	% K(a)	% Na(a)	STY	% Selectivity	Washing Liquids and Sequence
<u>Sodium Reduced - "Series A"</u>					
V-1*	2.83	0.518	527	93.7	5x H2O
V-2A	2.87	0.268	603	93.3	3x H2O plus 2x 5% KOAc
V-3A	2.88	0.249	615	93.2	2x H2O plus 3x 5% KOAc
V-4A	2.90	0.258	630	93.2	1x H2O plus 4x 5% KOAc
V-5A	2.94	0.247	604	93.3	3x H2O plus 2x 10% KOAc
V-6A	2.95	0.181	571	93.5	2x H2O plus 3x 10% KOAc
<u>Sodium Reduced Then Added - "Series B"</u>					
V-1*	2.83	0.518	527	93.7	5x H2O
V-2B*	2.84	0.554	516	93.6	3x H2O plus 2x 5% KOAc
V-3B*	2.85	0.558	519	93.9	2x H2O plus 3x 5% KOAc
V-4B*	2.86	0.561	534	93.5	1x H2O plus 4x 5% KOAc
V-5B*	2.90	0.567	502	93.8	3x H2O plus 2x 10% KOAc
V-6B*	2.90	0.574	488	94.1	2x H2O plus 3x 10% KOAc

(a) Estimated value. Calculated from the AA Analysis prior to KOAc/NaOAc impregnation and the quantities of acetates added.

* Comparative Examples

Significant activity improvements are seen in Table J in the "Series A" catalysts (compare Run V-1 with Runs V-2A through V-6A) and these improvements are in general agreement with the lower sodium contents of these catalysts. The "Series B" catalysts show that the readdition of sodium to "Series A" catalysts suppresses catalyst activities back to the range of the original, water-washed catalyst (compare Run V-1 with Runs V-2B through V-6B). These results again support the theory that removal of sodium is responsible for the observed activity gains.

EXAMPLE VI

Ion chromatography was used to analyze the effluents from the Column Washing Procedure and Batch Washing Procedure from several catalyst preparations. These involved the use of both water and potassium acetate solutions as the wash liquids and were done in an effort to detect any impurity which might go undetected by ICP analyses. Sulfate appeared to be the major impurity, yet was estimated to be less than 100 ppm in the original catalyst. Smaller levels of phosphate and chloride were also detected. To determine whether sulfate might have a detrimental effect on activity, potassium sulfate was added in amounts of 500 and 1000 ppm to two catalysts. The effect on activity was insignificant as is shown in Table K.

TABLE K

Effect of Added sulfate		
Sulfate(a)	STY	% Selectivity
0	550	93.8
500	552	93.9
1000	577	93.8

(a) ppm of potassium sulfate added with the potassium acetate promoter.

Examples VII to XII below illustrate the preferred embodiment of this invention that is shown in Figure 3.

Example VII:

Using the Catalyst Preparation Procedure, a catalyst was prepared on 50 g of Support I using sodium hydroxide as the precipitating agent. After the reduction step, the liquid was drained from the catalyst and the beads were rinsed four times with water to remove metal sludge. The damp catalyst was divided into three equal portions labeled Samples A, B, and C. Samples B and C were retained for use in the following Examples. Sample A was washed five times with 23-ml quantities of 5% potassium acetate solution for a total of 8 hours using the Batch Washing Procedure of Run IV-4 above. Each wash was of 96 minutes duration. The catalyst was dried at 60 °C without rinsing with water, and evaluated for vinyl acetate activity without further addition of potassium acetate. The analysis and test results are shown in Table L.

Example VIII:

Sample B prepared in Example VII above was washed as described in that Example, except that the first four washes with 5% potassium acetate had a duration of 1 hour each and the final wash had a duration of 4 hours. The catalyst was dried at 60 °C without rinsing with water. The analysis and test results are shown in Table L.

Example IX:

Sample C prepared in Example VII above was washed as described in that Example, except that 7% potassium acetate solution was used. The catalyst was dried at 60 °C without rinsing with water. The analysis and test results are shown in Table L.

Comparative Example X:

A 20-liter quantity of catalyst was prepared in a pilot plant using the Catalyst Preparation Procedure and water washed using the Batch Washing Procedure. The analysis and test results are shown in Table L.

Example XI:

A 20-liter catalyst sample was prepared using the process described in Example VII above. The analysis and test results are shown in Table L.

Example XII:

A 520-liter catalyst sample was prepared in a commercial production unit using the process described in Example VII above. The analysis and test results are shown in Table L.

TABLE L

Performance of Catalysts Prepared Using the Five-Step Preparation Procedure					
RUN	% Pd	% Au	% K	% Na	STY
IV-3*	0.54	0.19	2.2	0.47	535
VII	--	0.20	2.5	0.10	643
VIII	0.57	0.22	2.5	0.11	645
IX	0.56	0.22	2.9	0.10	592
X*	0.53	0.20	2.3	0.73	587
XI	0.56	0.26	2.9	0.12	695
XII	0.56	0.25	3.0	0.18	666

*Comparative Examples (seven-step preparations)

The data in Table L shows the improvements achieved with this invention.

Example XIII:

A sample of catalyst from Example XII above was impregnated with potassium acetate solution at a concentration calculated to increase the potassium loading by about 0.8%. The resulting catalyst contained 0.56% Pd, 0.25% Au, 3.7% K and 0.17 Na % and had an STY of 550.

The purpose of Examples XIV to XXIV below was to demonstrate the utility of various cation exchange solutions in Embodiment C of this invention.

Comparative Example XIV:

A catalyst was prepared using the catalyst preparation procedure with 90 grams of support and sodium hydroxide as the precipitating agent. Following the reduction step, the catalyst was drained and the beads were rinsed four times with water. The damp catalyst was divided into six equal portions labelled Samples A, B, C, D, E and F. Samples B through F were retained for use in the examples which follow. Sample A was washed with five 20-ml portions of water using the Batch Washing Procedure as set out in Run IV-3 above. Evaluation of the finished catalyst gave the results shown in Table M.

Example XV:

Sample B from Example XIV above was washed with 20-ml portions of 2% ammonium carbonate in water using the procedure described in that Example. Evaluation of the finished catalyst gave the results shown in Table M.

Example XVI:

Sample C from Example XIV above was washed with 20-ml portions of 2% lithium acetate in water using the procedure described in that Example. Evaluation of the catalyst gave the results shown in Table J. The lithium content of the finished catalyst was found to be 0.18% by AA analysis.

Comparative Example XVII:

Sample D from Example XIV above was washed with 20-ml portions of 2% sodium acetate in water using the procedure described in that Example. Catalyst evaluation gave the results in Table M.

Example XVIII:

Sample E from Example XIV above was washed with 20-ml portions of 2% potassium nitrate in water using the procedure described in that Example. Catalyst evaluation gave the results in Table M.

Example XIX:

Sample F from Example XIV above was washed with 20-ml portions of 2% potassium carbonate in water using the procedure described in that Example. Results of catalyst evaluation are shown in Table M.

TABLE M

Effect of Various Cation Exchange Solutions on Catalyst Activity						
Example	Salt	%Pd	%Au	% K	%Na	STY
XV*	None	0.58	0.22	2.23	0.37	474**
XVI	(NH ₄) ₂ CO ₃	0.58	0.22	2.20	0.13	527
XVII	LiOAc	0.58	0.23	2.22	0.19	486
XVIII*	NaOAc	0.57	0.22	2.26	0.79	447
XIX	KNO ₃	0.59	0.23	2.26	0.13	492
XX	K ₂ CO ₃	0.59	0.23	3.06	0.14	523

* Comparative Examples

** Average of three runs having STY's of 453, 498 & 470.

Comparative Example XX:

Catalysts were prepared according to the procedure of Example XV above. Following reduction, the damp catalyst was divided into six equal portions labelled Samples A, B, C, D, E, and F. Samples B through F were retained for use in the Examples which follow. Sample A was washed with five 20-ml portions of water as described in Example XV above. Catalyst evaluation gave the results shown in Table N.

Example XXI:

Sample B from Example XXI above was washed with 20-ml portions of 2% ammonium acetate in water as described in Example XV above. Catalyst evaluation gave the results shown in Table N.

Example XXII:

Sample C from Example XXI above was washed with 20-ml portions of 2% potassium acetate in water as described in Example XV above. Catalyst evaluation gave the results shown in Table N.

Example XXIII:

Sample D from Example XXI above was washed with 20-ml portions of 2% potassium sulfate in water as described in Example XV above. Catalyst evaluation gave the results in shown Table N. The potassium sulfate solution is a less suitable cation exchange solution because it apparently converts to the effective species (potassium acetate) relatively slowly.

Example XXIV:

Sample F from Example XXI above was washed with 20-ml portions of 2% magnesium acetate in water using the procedure described in Example XV. Catalyst evaluation gave the results shown in Table N.

TABLE N

Effect of Various Cation Exchange Solutions on Catalyst Activity						
Example	Salt	% Pd	% Au	% K	% Na	STY
XXI*	None	0.560	0.196	2.27	0.52	523
XXII	NH ₄ OAc	0.576	0.187	2.49	0.11	594
XXIII	KOAc	0.613	0.209	2.13	0.13	561
XXIV	K ₂ SO ₄	0.618	0.216	2.13	0.12	493**
XXV	Mg(OAc) ₂	0.573	0.225	2.39	0.17	575

* Comparative Examples

** There was insufficient reaction time to show the effectiveness of this cation exchange solution.

CATALYST COMPOSITIONS OF INVENTION

The catalysts of this invention produced by any of the above embodiments (i.e., Embodiments A, B or C) are useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and comprise support particles which are capable of exchanging cations and which are impregnated with precipitated and reduced palladium and gold and a potassium promoter, any sodium in the catalyst being present in an amount desirably no more than 0.3 weight percent based on the total weight of the catalyst.

The catalysts of this invention produced by any of the above embodiments preferably have a palladium content of greater than 0.25 weight percent based on the total weight of the catalyst, more preferably greater than 0.5 weight percent based on the total weight of the catalyst and most preferably from 0.5 to 1.7 weight percent based on the total weight of the catalyst. It is preferred that the gold to palladium weight ratio of the catalyst is from 0.2 to 1.5 and, most preferably, from 0.4 to 1.2.

It is preferred that the catalysts of this invention produced by any of the above embodiments are shell-impregnated catalysts wherein a catalyst support has a particle diameter from about 3 to about 7 millimeters and a pore volume of 0.2 to 1.5 milliliters per gram. The palladium and gold are preferably distributed in the outermost 1.0 millimeter thick layer of the catalyst support particles. The catalysts preferably contain from about 1.4 to about 3.8 weight percent (more preferably from 2 to 3.6 weight percent) of potassium derived from the potassium promoter.

The catalysts of this invention produced by any of the above embodiments have reduced sodium contents. Preferably, the catalysts contain no more than 0.3 weight percent sodium based on the weight of the catalyst. More preferably, the catalysts contain no more than 0.2 weight percent sodium and, most preferably, the catalysts contain no more than about 0.1 weight percent sodium based on the weight of the catalyst. The amount of sodium in the catalysts of this invention will depend upon such factors as the starting materials used, the number of washes, the total wash time, the volume of washing solutions and the concentration of the cation in the cation exchange solution.

The catalysts of this invention produced by any of the above embodiments can be produced by the above-described process of this invention and by the processes described in the two above-mentioned U.S. patent applications filed concurrently here with.

PROCESS OF INVENTION FOR PRODUCING ALKENYL ALKANOATES

The process of the present invention for producing alkenyl alkanoates comprises reacting an alkenyl, an alkanolic acid, and an oxygen-containing gas in the presence of a catalytic amount of catalyst of this invention as described above. The process is preferably conducted at a temperature from 100 °C to 250 °C (and most preferably at a temperature from 140 °C to 200 °C) and at a pressure from 15 psi to 300 psi (most preferably at a pressure from 90 pounds per square inch to 150 pounds per square inch.) The process is preferably conducted continuously in the vapor phase.

The process of this invention for producing alkenyl alkanoates is characterized by the greater activity of the catalyst. Typically the activity of the catalysts is 5% to 25% greater (in terms of quantity of alkenyl alkanoate produced per unit of catalyst per unit time) as compared to otherwise identical catalysts containing from over 0.3 to about 1.0 weight percent sodium. Although catalyst selectivity (i.e., the tendency

to produce alkenyl alkanoates rather than by-products such as carbon dioxide) declines somewhat with decreasing sodium content, that disadvantage is more than offset by increased catalyst activity, particularly in the range of sodium contents found in commercial alkenyl alkanoate catalysts (e.g., up to about 1.0 weight percent sodium).

5 Preferred alkanolic acid starting materials used in the process of this invention for producing alkenyl alkanoates contain from two to four carbon atoms (e.g., acetic, propionic and butyric acid). Preferred alkene starting materials contain from two to four carbon atoms (e.g. ethylene, propylene and n-butene). Preferred products of the process are vinyl acetate, vinyl propionate, vinyl butyrate, and allyl acetate.

One aspect of the process of this invention for producing alkenyl alkanoates involves the use of the models shown in Table G below to predict the oxygen conversion to vinyl acetate, the activity of the catalyst, the selectivity of the catalyst to vinyl acetate, the production of ethyl acetate by-product and/or the production of heavy by-products.

The alkenyl alkanoates produced by the process of this invention are known compounds having known utilities (e.g., vinyl acetate is useful in producing polyvinyl acetate).

15 Claims

1. A process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate, said process comprising increasing the activity of the catalyst by reducing its sodium content.

2. A process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate, said process comprising the steps of:

(a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;

(b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;

(c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent;

(d) washing the support particles with water;

(e) drying the support particles;

(f) further impregnating the support particles with a potassium promoter; and

(g) drying the impregnated particles to produce the catalyst; and

said process being conducted by employing essentially sodium-free starting materials in steps (b) and (c) so as to reduce the amount of sodium in the catalyst and thereby to increase the activity of the catalyst.

3. A process as claimed in claim 2 wherein potassium hydroxide is used as the precipitating agent in step (b) and wherein potassium salt is used to aid in the displacement of sodium bound on the carrier by the potassium precipitating agent.

4. A process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate, said process comprising the steps of:

(a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;

(b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;

(c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent;

(d) washing the support particles with water;

(e) drying the support particles;

(f) further impregnating the support particles with a potassium promoter; and

- (g) drying the support so impregnated to produce a dried catalyst containing sodium owing to the presence of sodium in one or more of the materials used in steps (a) to (f),
 (h) washing the dried catalyst with water or with an aqueous solution containing a potassium promoter so as to reduce the amount of sodium in the catalyst and thereby to increase the activity of the catalyst, and
 (i) drying the catalyst.
- 5
5. A process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate, said process comprising the steps of:
- 10
- (a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;
- (b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;
- 15
- (c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent so as to produce an impregnated support containing sodium owing to the presence of sodium in one or more of the materials used in steps (a) to (c);
- (d) washing the impregnated support particles with a cation exchange solution so that the amount of sodium in the catalyst is reduced and the activity of the catalyst is increased; and
- 20
- (e) drying the washed impregnated support particles to produce the catalyst.
6. A process for producing a catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce a alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with palladium, gold and potassium acetate, said process comprising the steps of:
- 25
- (a) impregnating the support particles with aqueous solutions of water-soluble palladium and gold compounds;
- (b) precipitating water-insoluble palladium and gold compounds onto the support particles from such solutions using a precipitating agent;
- 30
- (c) converting the precipitated water-insoluble palladium and gold compounds to palladium and gold on the support particles using a reducing agent, said impregnated support containing sodium owing to the presence of sodium in one or more of the materials used in steps (a) to (c);
- (d) washing the support particles with a potassium promoter solution in a concentration and in an amount sufficient both: (I) to reduce the amount of sodium in the catalyst so as to increase the activity of the catalyst, and (II) to impregnate the catalyst with the amount of potassium necessary to further promote the activity of the catalyst; and
- 35
- (e) drying the washed and further impregnated support particles to produce the catalyst.
- 40
7. A process as claimed in claim 6 wherein the potassium promoter solution is an aqueous potassium acetate solution.
8. A catalyst that is useful in catalyzing the reaction of an alkene, an alkanolic acid and an oxygen-containing gas to produce an alkenyl alkanoate and that comprises support particles which are capable of exchanging cations and which are impregnated with precipitated and reduced palladium and gold and a potassium promoter, any sodium in the catalyst being present in an amount no more than 0.3 weight percent based on the weight of the catalyst.
- 45
9. A catalyst as claimed in claim 8 wherein any sodium in the catalyst is present in an amount no more than 0.2 weight percent based on the weight of the catalyst.
- 50
10. A process for producing an alkenyl alkanoate which comprises reacting an alkene, an alkanolic acid and an oxygen-containing gas in the presence of a catalytic amount of a catalyst as defined in claim 8 or claim 9.
- 55

Figure 1
Predicted Effect of
Sodium on Performance

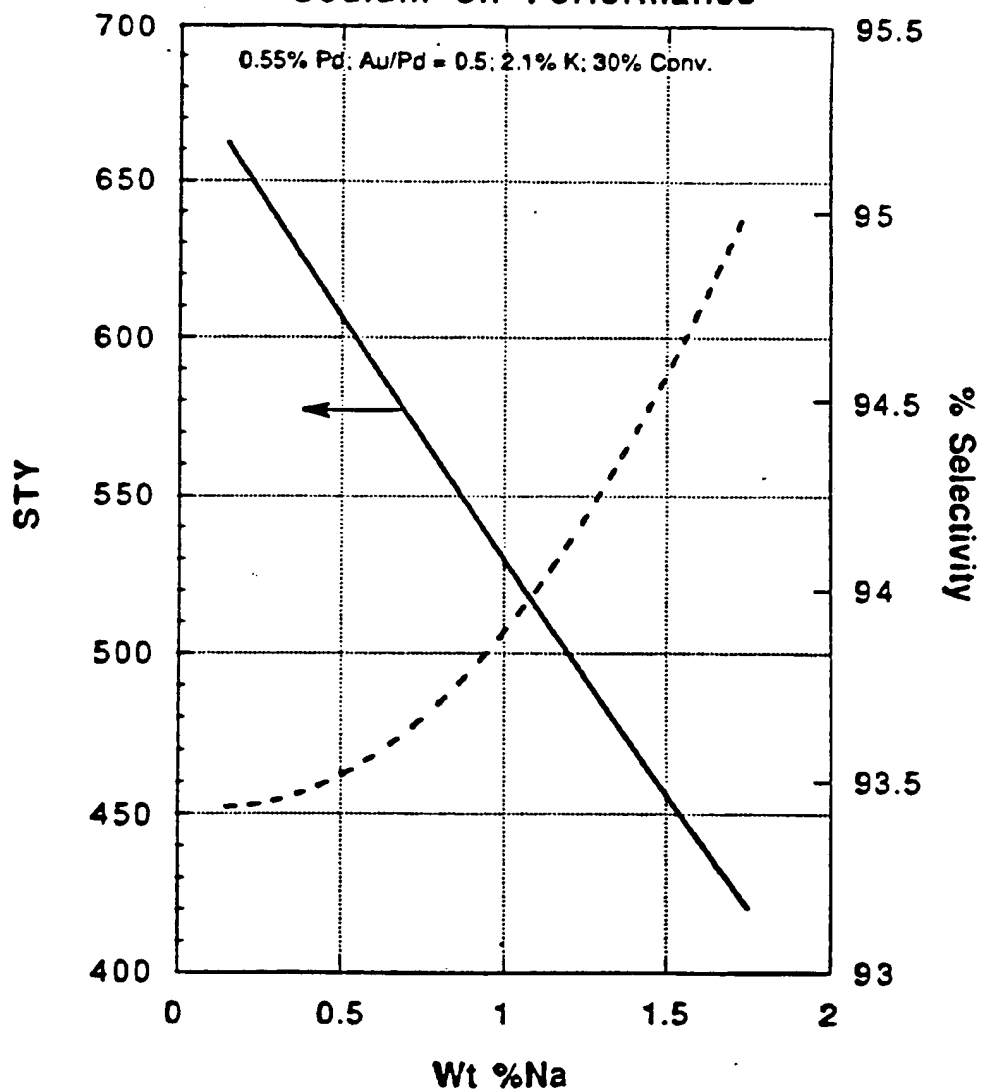
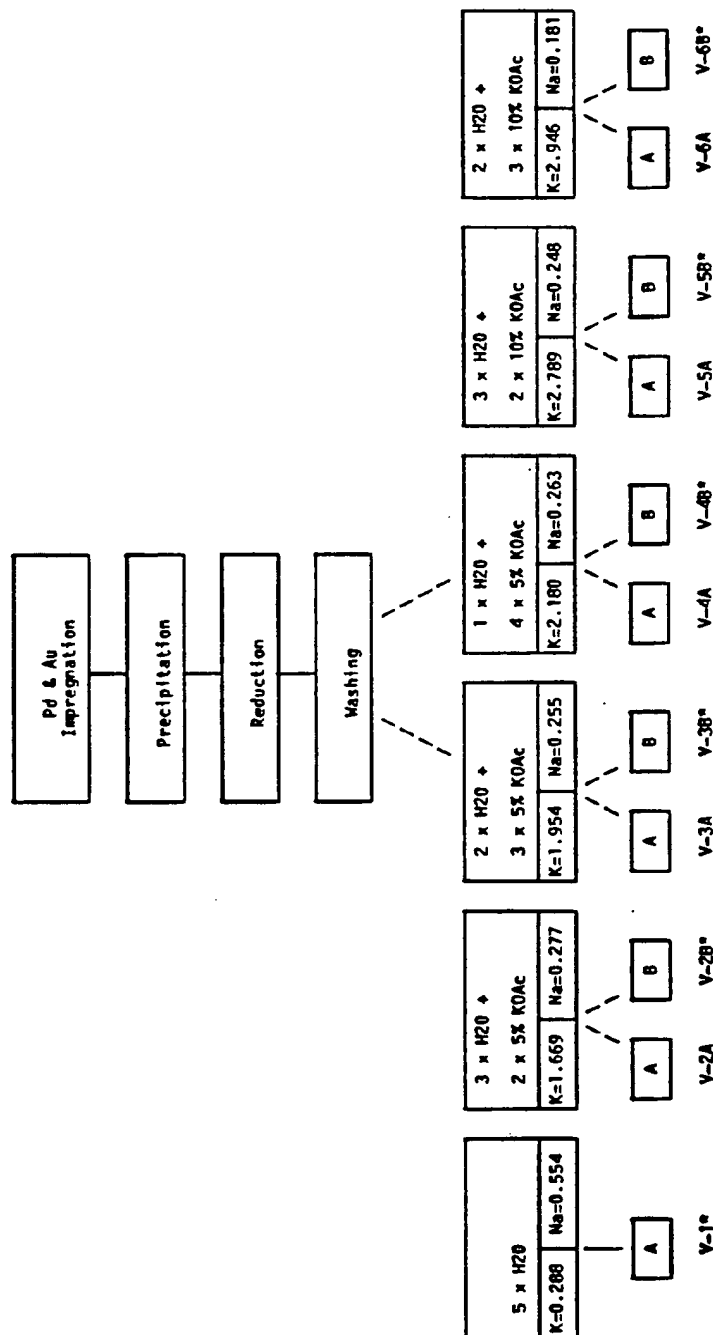


FIGURE 2

BATCH-WASHING STUDY[#]

A = Impregnation with KOAc to a target value of 2.9% K in the finished catalyst. No Sodium added.

B = Impregnation with KOAc and NaOAc to give values of 2.9% K and 0.55% Na in the finished catalyst

K and Na values are the wt% potassium and sodium, respectively as determined by AA analysis of the washed catalyst.

* Comparative Examples

Drying steps not shown

Figure 3
Comparison of
Catalyst Preparation Procedures

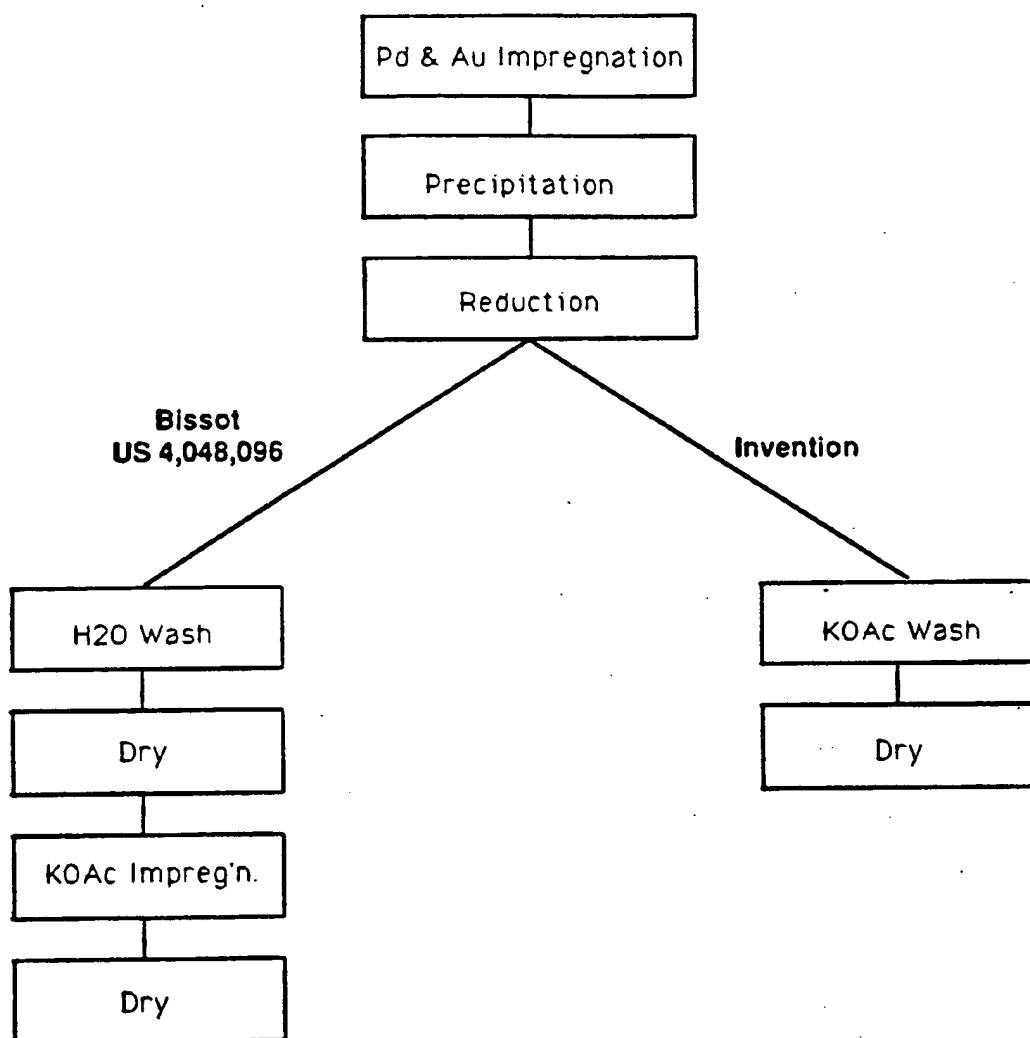
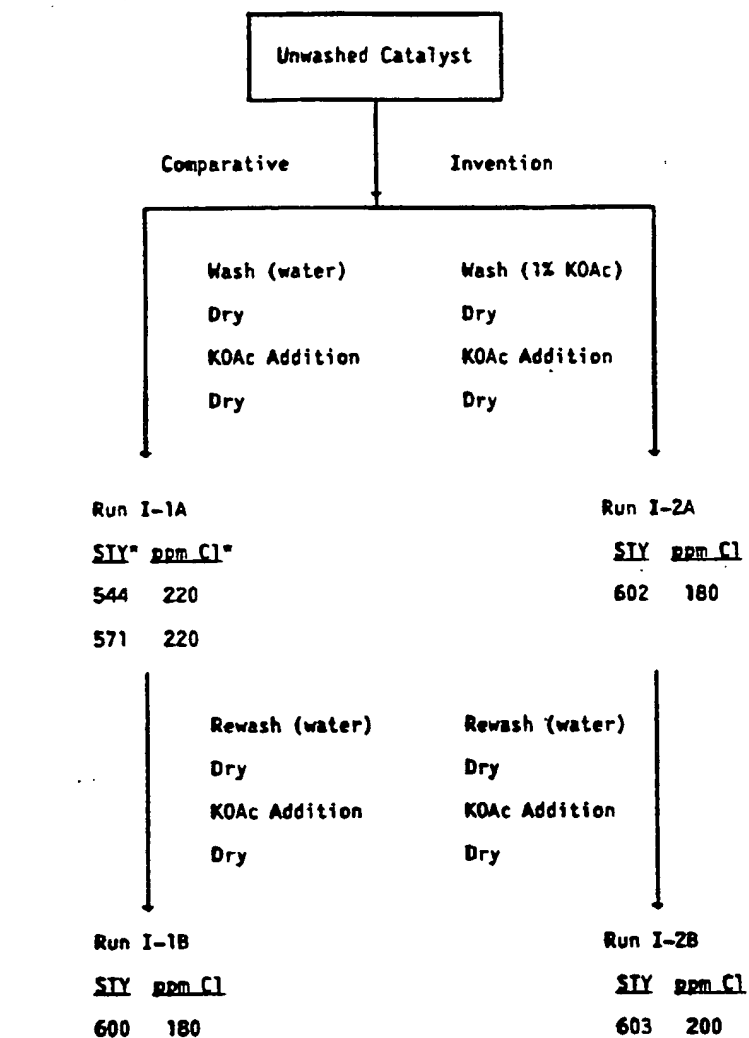


FIGURE 4

EFFECT OF WASHING PROCEDURE
ON CATALYST ACTIVITY



*Duplicate Tests Conducted



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 5469

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, Y	US-A-4 048 096 (T. BISSOT) * claim 1 *	1, 8-10	B01J23/52 B01J31/04 B01J37/02
Y	US-A-3 923 688 (J. HAMMEL) ---	1, 8-10	B01J37/06 B01J67/055
A	US-A-3 761 513 (K. SENNEWALD) ---		
A	GB-A-1 500 167 (BAYER) ---		
A	EP-A-0 403 950 (HOECHST) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B01J C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 JANUARY 1993	Examiner THION M.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons @ : member of the same patent family, corresponding document			

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.